EFFECT OF LOW COST ADDITIVES ON ENHANCEMENT OF GAS IN ANAEROBIC DIGESTION

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by
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to the

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POST GRADUATE OFFICE
Submitted on.....

To

my ever-loving
elder brother
Padam Chand
my wife
Neelu
and son, Ankit.

POST GRADUATE OFFICE
This thesis has been approved
for the award of the Degree of
Master of Technology (M Tech.)
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CERTIFICATE

Certified that the work presented in this thesis entitled "Effect of Low Cost Additives on Enhancement of Gas in Anaerobic Digestion" by Shri Anil Kumar Jain has been carried out under my supervision and it has not been submitted elsewhere for a degree.

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NOMENCLATURE

μ	Specific growth rate of biomass, time^{-1}
μ_m, μ_{max}	Maximum specific growth rate, time^{-1}
S	Steady state effluent substrate concentration, mass volume^{-1}
K_s	Saturation constant, mass volume^{-1}
k	Maximum specific substrate utilisation rate, time^{-1}
x	Active biomass concentration, mass volume^{-1}
q	Specific substrate utilisation rate, time^{-1}
Y	Growth yield
K_d	Microorganism decay coefficient, time^{-1}
θ^m, θ_c^m	The minimum biological solids retention time
S_o	Influent waste concentration, mass volume^{-1}
S_e	Effluent waste concentration, mass volume^{-1}
V	The volume of the reactor, volume
Q	The rate of raw wastewater flowing to the tank, volume time^{-1}
K_c	K_s for all fatty acids found or produced in the waste
B	Methane yield, volume CH_4 mass^{-1} COD added
G_s	Volumetric methane yield, volume CH_4 volume^{-1} fermenter time^{-1}
B_o	Ultimate methane yield, volume CH_4 mass^{-1} COD added
K_H	Kinetic parameter
G_{max}	Maximum volumetric methane production rate, volume CH_4 volume^{-1} fermenter time^{-1}
θ_{Gmax}	The detention time at which maximum volumetric methane production rate will occur, time
θ	Hydraulic retention time (HRT), time
θ	

ABSTRACT

Enhancement of methane production while treating high BOD wastes anaerobically, was possible when additional surface was provided by the addition of low cost granular additives such as cinder, and rashing rings (RR) whereas the addition of fine additives like bituminous coal powder (BCP) and coconut shell powder (CSP) was not much effective. 2 to 4 times higher methane production was possible, in the systems where granular additives were available for the growth of microbes, in comparison to the system without additives. The quantity of methane obtained was 81 percent of the theoretically estimated values per Kg of chemical oxygen demand (COD) destroyed. The ratio of biological solids retention time to hydraulic retention time (HRT) (θ_c/θ) was found to be 9.81 to 12.1 in systems containing granular media. The process stability was better because of low volatile fatty acids (VFA) levels in the systems containing coarse additives as compared to fine additives or control. The COD removal in case of cinder and RR containing digesters, was found to be 83 percent at a load of 7.5 Kg COD/m^3/day, whereas, maximum gas was obtained at a load of 12.5 Kg COD/m^3/day. The kinetic constants evaluated for design of reactors obtained from VFA, COD and gas data showed the maximum specific growth rate, yield coefficient and decay rate to be same for a particular substrate irrespective of the area available for the growth of microbes.

1. INTRODUCTION

With the march of civilization and industrial revolution, there has been an incessant demand for the energy and better environment. Declining reserves of oil and natural gas have necessitated the search for alternative raw material to replace petroleum. In the words of Francis Bacon, "He who will not apply new remedies must expect new evils". Industrial, municipal and agricultural residues represent significant biomass resources which will not only act as substitutes for petroleum but will also create a better harmony between man and environment. According to Jacob Rosin and Max Easuman "... as the chemical knowledge grows, we continue to discover that the useless rubbish of yesterday becomes the valuable resources of today".

Biological processes have been and will continue to be one of the most economical means of treatment of waste. Controlled anaerobic treatment processes are being considered today as one of the possible means of recovering energy in the form of methane gas, while at the same time reducing the pollutional load of organic wastes. The increasing popularity can be attributed partly to the fact that anaerobic treatment combines a number of important benefits with a few, if any, insurmountable drawbacks over conventional aerobic process.

Approximately 11×10^6 KJ equivalent of methane (CH_4) is produced synthesising biomass of 10 to 50 Kg (dry mass) per ton of chemical oxygen demand. In contrast aerobic

treatment processes consume approximately 500 Kg of biomass per ton of COD removed (Chou et al., 1978). The net operating cost difference is approximately $160 less for anaerobic process over aerobic process per ton of COD treated (assuming $0.06/kwh, $4.50/$10^6$ kJ for methane recovered and $100/ton of dry cell mass disposal costs). This cost difference may be as high as $250 for some industries (McDermott, 1983).

The basic question is no longer whether an industrial or municipal waste can be anaerobically biodegraded to methane, since most organics are amenable to anaerobic treatment, but rather at what rate it is degradable, to what degree it is degradable and also how maximum the yield of methane can be obtained? These and other relevant questions must now be addressed for the rational exploitation of the process. The design, operation and the economy of anaerobic process are the three factors which are closely interlinked, and in one way or another all are related to a number of external factors.

Sugar and distillery industries are among the major polluters of the environment in U.P. Of the 180 sugar mills in the country, 73 are located in this state. These industries produce large quantities of effluent with very high soluble biochemical oxygen demand (BOD) in the form of molasses. Although, molasses is a raw material for the distillery products, but at places where transportation cost of molasses is inhibitive for its use in distillery, besides handling and spillage problems, it appears

to be appropriate to utilise molasses itself as raw material to produce gas by anaerobic digestion. The high BOD value, and easy solubility of molasses in water, makes it suitable for this process.

In the present investigation, an attempt was made to treat an industrially produced complex substrate (molasses) effectively in terms of enhanced gas production and better effluent, by anaerobic oxidation using fine materials like coconut shell and coal powder and coarse materials like cinder and rashing rings to provide surface for the growth of microorganismsto evaluate kinetic parameters for the design of anaerobic digesters operating under these conditions. Semi-continuous digesters system without recycle was used. Glucose as simple substrate has been used for comparison.

2. LITERATURE REVIEW

The 'energy crises' of 1973 is an important land-mark in human history as it triggered the search for new and unconventional energy sources. "No energy is more expensive than no energy", in the words of late Dr. Homi Bhabha. With near exhaustion of the world's readily available fossil fuel at hand and high prices of crude oil and natural gas have necessitated the search for alternative raw materials to replace petroleum. Much work has been done in the last decade on the feasibility of developing biomass to energy processes. 'Biomass' has received near universal recommendation as an efficient energy source and this "appropriate technology" is close to the heart of the third world countries. Another advantage associated with it is the protection of our environment. Microbiological formation of methane has been occurring naturally for ages in such diverse habitats as marshes, rice paddies, benthic deposits, deep ocean trenches, trees, cattle, pigs waste etc. (Boon, 1974; Balch et al., 1979). The use of methane as energy source was known about four thousand years ago also. Much research has been carried out in the last 70 years in an attempt to understand the behaviour of those bacteria which produce methane. The methane producing bacteria grow and liberate energy under anaerobic conditions. In the past five years, there has been a upsurge in research interests specifically in methane bacteria. This supported by advances in process engineering has been translated into numerous

treatability studies of various industrial wastewaters. Many anaerobic process configurations have found widespread usage in the treatment of municipal sludges and in the treatment of organic industrial wastes like, sugar and distillery industry wastes, tannery wastes, slaughter-house waste, and animal manure slurries (Grasius, 1983, Carrondo et al., 1983; Braun et al., 1982; Landina et al., 1982; and Chen et al., 1980).

The common alternative to anaerobic biotechnology for treatment of industrial wastewater is the aerobic biological process. Some significant advantages of anaerobic stabilisation process over aerobic process are higher organic loading potential, as the process is not limited by the oxygen transfer capability at higher oxygen utilisation rate, low production of biological solids as a result of minimal energy available for microbial growths, generation of methane gas and minimum requirement of energy input. The potential market for anaerobic biotechnology is vast, but a sizeable hurdle of user confidence must be overcome to win that market. The improved understanding of microbial consortium involved and significant development in reactor design are now laying a strong foundation for development of efficient and reliable anaerobic biotechnology for treatment of wide variety of industrial wastes.

2.1. Microbiology and Biochemistry of Anaerobic Systems

The anaerobic digestion process is dependent on various microorganisms and thus it becomes essential to know

Anaerobic digestion involves microbial conversion of organic matters to methane (CH_4) and carbon dioxide (CO_2) in the absence of molecular oxygen. Organic wastes are introduced continuously or intermittently and retained in the reactor for varying periods of time. The stabilised sludge, which is withdrawn from the process is nonputrescible. The process is mediated by different groups of facultative and obligate anaerobic organisms. Methanogenesis is generally the slowest step in anaerobic digestion and is hence the rate limiting step. There should be a balance maintained between the fast growing acid formers and the fastidious methanogens for the process to be stable.

2.1.1. Multi-step Methanogenesis

Anaerobic digestion has been classified as a three step process. In the first step, complex organic materials like carbohydrates, proteins, and lipids are hydrolysed and fermented to fatty acids, alcohals, carbon dioxide and ammonia and to hydrogen which originates from formic acid and the oxidation of ferrodoxin. The liquefaction of the solid organic compartments represents the rate limiting step in this first stage of breakdown in which most of the anaerobic and facultative anaerobic fermenting organisms are involved.

In the second step, the organic products of the first step are converted into acetic acid, hydrogen and carbon dioxide. This process is controlled by the actual hydrogen tension which plays an important role in the regulation of anaerobic digestion of dissolved organic matter. Thus the

fermentation products would accumulate if hydrogen were not removed. The reduction of protons, that is hydrogen production, is essential to these organisms, whereas it is not for those of the first step. Therefore this group of organism can be called as obligate proton reducing acetogens. Acetogens, because the second obligate end product of their metabolism, in this step, is acetate.

The third step is distinguished by the production of methane, in which acetate and H_2 and CO_2 are converted to methane by methanogenic bacteria.

2.1.2. Microbiology

The current biological model of a methanogenic mixed culture digestion consist of four trophic groups of bacteria. These four trophic groups form a food chain with the final end products containing the products CO_2 and CH_4. The characteristics of these trophic groups of bacteria is discussed in brief.

2.1.2.1. Acidogenic Bacteria

The acidogenic population is by far the largest of the trophic groups of bacteria. Many of these bacteria have large substrate ranges and short generation times (Forday and Greenfield, 1983). The principal intermediates produced by these bacteria are the short chain carboxylic acids, i.e. volatile fatty acids. The primary acids produced are acetic, followed by propionic and butyric with small quantities of formic, valeric, isovaleric and caproic acids are also produced. Many of these bacteria in the presence of hydrogen consuming bacteria (methanogenic,

homoacetogenic and sulphate reducing bacteria) produce hydrogen for the disposal of excess electrons generated during the energy yielding oxidations of organic materials. However, excessive activity of the acidogenic population can result in digester failure. Unionised organic acids, hydrogen ions and hydrogen are inhibitory to other groups of bacteria while the acidogenic population is much more tolerant to these intermediates. It has been established that most of the acidogenic bacteria are strict anaerobes (Forday and Greenfield, 1983).

2.1.2.2. Acetogenic Bacteria

The acetogenic bacteria obtain their energy from the oxidation of organic acids and alcohols and, in contrast to the hydrogen forming acidogenic bacteria, these bacteria have an obligate requirement for disposal of electrons as hydrogen gas. Growth of the acetogenic bacteria can occur only at partial pressures of hydrogen less than 10^{-5} of an atmosphere. The conversion of these higher volatile fatty acids butyrate and propionate, to methanogenic substrate, hydrogen and acetate, is an important step in the digestion process, as the unionised forms of these acids are particularly toxic to the methanogenic bacteria. The acetogenic bacteria are the slowest growing of the trophic groups and hence represents the rate limiting step in the methanogenic processes. Inhibition of the acetogenic population, for example, due to hydrogen accumulation will result in an environment unfavourable for the methanogens (Forday and Greenfield, 1983).

2.1.2.3. Methanogenic Bacteria

The methane forming bacteria are a diverse group of rod, spherical and spiral shaped organisms showing considerable intra-species variations in cell dimension and organisation (Zeikus JG, 1980). They are obligate anaerobes. They are particularly sensitive to pH values above 7.5 and below 6.0 and are inhibited by unionised volatile fatty acids. All species of methanogens can grow autotrophically on H_2 and CO_2 as sole energy and carbon sources. A few species can utilise formate. Acetate utilisation is restricted only to strains of Methanosarcina barkeri (Mosey, 1982), and this species has been found to be the predominant methanogen in anaerobic digesters. About 70-72 percent methane generated in digestion is derived from acetate and the remaining 28 to 30 percent is from H_2 and CO_2 (Mosey, 1983; Speece, 1983; Forday and Greenfield, 1983; Harremoes and Henze, 1982). The hydrogen utilising bacteria can be represented by Methanospirillium hungatei (Mosey, 1983). The growth efficiencies of the methanogens appear greater than that of certain species of obligate anaerobes (e.g., the homoacetogens) or obligate aerobes that metabolise unicarbon compound. Sulphur reducing bacteria, are regarded as major sink for hydrogen in methanogenic systems. In pure culture, the growth yield of Methanosarcina barkeri on H_2 and CO_2 is four times greater than that on acetate.

2.1.2.4. Homoacetogenic Bacteria

The significance of the homoacetogenic bacteria in the methanogenic process is not fully

understood (Forday and Greenfield, 1983). They contribute to the acetate pool via carbohydrate degradation. They can also donate hydrogen to the methanogenic bacteria by a phenomenon known as interspecies hydrogen transfer. Some species are able to convert H_2 and CO_2 to acetate. Recently, one species Acetobacterium woodii has been shown to be able to degrade aromatic compounds (Bache and Pfenning, 1981). Their significance as hydrogen consumers under normal conditions is considered to be minor as they are unable to compete with the methanogenic bacteria (Zeikus, 1980). They may, however, be important in maintaining low hydrogen partial pressures during perturbations in the digester which temporarily inhibit the methanogens.

2.1.3. Biochemistry of Methanogenesis

In the actual stabilisation stage, methane is produced in two ways, one is from carbon dioxide-molecular hydrogen and the next from acetic acid. The formation of methane from carbon dioxide-hydrogen was first observed by Sohngen in 1906 to proceed according to the following reaction:

$$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O \qquad 2.1$$

Later studies have demonstrated that this reaction pathway is the most preferred one, for energy production by methanogenic bacteria (Wise et al., 1978). Carbon dioxide is the most oxidised form of carbon, whereas, methane is the most reduced form. This reaction is mediated by an electron transport system involving dehydrogenese, electron carriers and four reductases (Thauer et al., 1977). The four reduction

steps gives rise to compounds at the oxidation level of formate, formaldehyde, methanol and finally methane. These intermediate represent only the oxidation state of the one carbon compound and not their free molecules. As electron carriers, besides coenzyme M, methane forming bacteria contain F420, a compound not found in any other organism. The later is a low-molecular-weight, around 630, anionic compound. Carbon dioxide reduction to methane is coupled with phosphorylation, and synthesis of ATP evidenced by growth of Methanobacterium thermoautotrophicum on carbon dioxide and hydrogen as sole carbon and energy source (Thauer et al., 1977).

Acetate is the precursor of about 70 percent of the methane formed in anaerobic environments. Through decarboxylation of acetate, methane and bicarbonates are produced as per following equation:

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \quad (\Delta G^\circ = -62 \text{ kJ}) \qquad 2.2$$

In the thermodynamic and mechanistic consideration, this reaction of decarboxylation of acetate does not release enough energy to synthesise ATP under standard and natural conditions, since the bicarbonate and methane concentration are relatively high. Moreover, it is not a redox reaction. Therefore, it was doubted whether this reaction is growth coupled (Toerien et al., 1971). The free energy for the conversion of acetate to methane is so low (-28 kJ/mol) that a debate over whether acetate could serve as the sole substrate for methanogens lasted for years (Zeikus et al.,(1975), and was finally demonstrated by Smith and Mah (1980) in pure

culture. This low free energy was considered inadequate for adenosine triphosphate (ATP) production, which is the energy source for bacterial metabolism. It is now suggested that ATP production in methanogenesis is coupled to electron transport instead of substrate-level phosphorylation (Thauer et al., 1977). However, mechanism coupling methane production and ATP synthesis still remain a mystery (Zeikus et al., 1977). But, Smith et al. (1980) report that, methanosarcina strain 227 growsrapidly and produced methane on a mineral medium containing acetate as the sole added organic substrate. Unequivocal evidence indicates, the cleavage of acetate to methane and carbon dioxide provides the energy for growth in the presence or absence of other organic compounds; These latter compounds do not serve as energy source, electron donors, or significant source of methane during this acetoclastic reaction. Their data rule out co-metabolism, acetate reduction, and acetate oxidation of carbon dioxide followed by carbon dioxide reduction to methane as a mechanism for growth on acetate. But, the mechanistic and thermodynamic problem raised by growth on acetate using a decarboxylation reaction remainsunsolved. Zehnder et al. (1980) could isolate, Methanobacterium soehngenii, a bacterium common in digested sludge, gram negative, nonmotile, straight rod with flat ends and forming filaments which grow to great lengths. They also report that, alongwith coenzyme M, F420 was present in the cell.

Zehnder et al. (1979) proposed two hypothetical mechanism for ATP formation in methanogenic bacteria by which

a proton motive force could be established in the absence of a redox reaction, using the energy released from the decarboxylation of acetate. In a flip-flop mechanisms a protein lying across the membrane binds an acetate molecule on the outside and a proton on the inside. The acetate is cleaved into methane and HCO_3^- and the energy released cause translocation of the proton inside the membrane to the outside. In the second mechanism, the difference in acidity between substrate and product establish a pH gradient. When the ionised acetate is transported in to the cell and splits to CH_4 and HCO_3^-, the pH in the cell rises due to the lower acidity of the HCO_3^- compared to acetate, and the resulting proton motive force can be used to drive ATP synthesis. Thus, they conclude, neither electron transport nor substrate level phosphorylation are needed to synthesise ATP.

Among the different microbial populationsinvolved in the various stages of waste stabilisation, the methanogenic group that degrade acetic acid, are the most important from the process kinetics point of view. As seen in reaction 2.2, the energy released being very less, the growth rate of the bacterium mediating the acetate splitting have very slow growth rate. The production of volatile fatty acid (VFA), ethanol and lactic acid are much faster than methane formation. However, in engineering practice the final step, that is, the methane fermentation from organic acids can be stated as the rate limiting step in the anaerobic process.

2.2. Process Stability and Environmental Factors

With anaerobic digesters operating experiences and their cost effectiveness have not been consistently good. Digesters are susceptible to malfunctioning. When the two main process, i.e., fermentation and methanogenesis occurs simultaneously, than process stability is dependent upon maintenance of a delicate biochemical balance between the fast growing 'acid formers' and the more fastidious 'methane formers'. Malfunctioning manifests itself in terms of reduced gas production, reduced degradation of organic materials and a simultaneous increase in acidity. Operational factors that have usually been associated with process failure include.

(i) Insufficient acclimation of methane formers to new substrates,

(ii) Nature, type and concentration of the pollutants (complexicity, composition, dissolved fraction)

(iii) Excessive concentration of ammonia, heavy metals, sulfides etc.

(iv) pH, temperature etc. (Lettinga et al., 1983).

Kotze (1968) monitored the enzymatic activity of anaerobic digesters receiving different substrates and concluded that adaptation to a substrate takes more than five weeks. Speece (1983) analysed that complex wastewaters containing organics have a continuous range of degradation rates, at low loading rates, the rate controlling step may be acid formation, as is evident by low volatile acids concentration. But as the loading rate increases the

methanogenesis stage may gradually become the rate controlling step, as evidence by an accumulation of volatile acids.

2.2.1. Effect of Nutrient Requirement and Trace Metals

Need of sufficient nutrients for the efficient working of anaerobic systems is well established. Nutrient such as nitrogen, phosphorus, certain heavy metals and cations are to be supplemented if not present in requisite quantities in the waste. A COD:N:P ratio of 400:7:1 is considered enough from N and P requirements. Sulphur is also essential and its requirement equals to that of phosphorus (Harremoes and Henze, 1982; Speece, 1983).

Most of the micronutrients, e.g., heavy metals beyond a certain minimum concentration results in severe toxicity. Also at higher concentrations, they become highly toxic, particularly to the methanogenic bacteria. Inhibitory and toxic levels of heavy metal, reported by Hayes and Theis (1978) for sewage sludge are given in Table 2.1. Inhibition levels were defined as those where gas production first declined and toxic levels were defined as causing a 70 percent reduction in gas levels. Iron, cobalt, nickel, sulfide have been shown to be obligatory nutrient requirement for methanogens to convert acetate to methane (Speece et al., 1983; Hoban and Vanden Berg, 1979). Hoban and Vanden Berg (1979) have also noted that iron is required by methanogens at unusually high levels. Dickert et al. (1981) state that the high contamination levels of a nickel in defined media is the reason why the nickel requirement for methanogens has

Table 2.1. Toxic and Inhibitory Levels of Heavy Metals in Anaerobic Digestion (Hayes and Theis, 1978)

Heavy metal	Step-fed		Pulse-fed toxic limit mg/l
	Inhibiting concentration mg/l	Toxic limit mg/l	
Cr(III)	130	260	<200
Cr(VI)	110	420	<180
Cu	40	70	<50
Ni	10	30	>30
Cd	-	>20	>10
Pb	340	>340	>250
Zn	400	600	<1700

long been overlooked. Specific addition of nickel to acetate utilizing methanogens has resulted in methane production rates in excess of 50 $Kg/m^3.d$, which is higher than any recorded in the literature (Speece, 1983). In spite of the fact that sulfide may adversely affect methane production by precipitating essential trace metals and that it is in itself toxic at concentration above 100 to 150 mg/l of unionized H_2S (Speece, 1983), sulfide is required by methanogens. Optimal sulfide concentrations reported in the literature for methanogenic growth vary from 1 to 25 mg/l (Scherer and Sahm, 1981). Molybdenum, tungsten and selenium have also been reported as required trace metals.

Ammonia formation results from the fermentation of nitrogenous compounds, such as proteins and urea. In anaerobic systems, ammonia is in equilibrium with ammonium ion or dissolved ammonia gas:

$$NH_4^+ = NH_3 + H^+ \qquad 2.3$$

The equilibrium products form an important buffer system in anaerobic digestion. In the treatment of waste containing low nitrogen:carbon ratios, all the ammonia from protein decomposition is recycled into cellular material, resulting in decreasedbuffer capacity and process instability. The toxicity of ammonia is also pH dependent as high pH will cause a shift in the above equilibrium to the more toxic free ammonia.

2.2.2. Temperature and pH Effect

Many biochemical and physical parameters are influenced by temperature. The three optimum ranges at which anaerobic digestion and other biological reactions occur are, thermophilic (50-65°C); mesophilic (20-45°C) and phychrophilic (20°C). In all the microbial system it is observed that temperature increase leadsto increased microbial activity. However, changes in overall process efficiency due to increased metabolic activities are balanced by a corresponding increase in the rate of microbial inactivation (Forday and Greenfield, 1983). Hence, the optimal temperature process represents the best compromise between the two factors. The required optimal design temperature can be

determined from laboratory scale experiments, since it may depend upon the waste to be treated.

The optimum pH range has been reported as 6.8-8.0 (Malina, 1962; Parker et al., 1981). The major controlling buffer in this pH range is the carbonate-bicarbonate system, with orthophosphoric acid, hydrosulfuric acid, volatile acid and ammonia contributing to pH stabilization. The sensitivity of anaerobic digestion to pH levels has been suggested to be a reflection of the pH sensitivity of the methanogenic population.

2.3. Attached Growth Anaerobic System

The conventional anaerobic systems employing suspended or diffused microbial system need to have very large reactor volume, because of low active biomass production in anaerobic digestion (Harremoes and Henze, 1982). By adopting attached growth system which can maintain high biomass concentration at relatively low hydraulic retention time (HRT-θ) in place of conventional suspended growth systems, results in lesser reactor volume. With the development of attached growth/fixed film reactors in anaerobic digestion, the present design configurations emables ratio of biological solids retention time (θ_c) to HRT(θ); θ_c/θ to be more. Since the higher biomass can be retained in this system, for a lower HRT it is possible to maintain the volatile fatty acids (VFA) levels to be low, hence, better pH control, which results in better process stability. In attached growth systems the basic principal is that microbes grow on some innert media (sand, glass, plastic, coal, synthetic

material etc.) by utilising the influent substrate. Studies have been carried out using activated carbon to find its effect on performance of reactors (McConville and Maier, 1978). Harremoes and Henze (1982), classify the reactors into categories like non-attached and attached growth systems and further subclassify them as per Table 2.2. The performance efficiency of biological reactor containing support particles depends upon.

(i) the number of support particles per unit reactor volume,

(ii) the average biomass hold up per particle,

(iii) the average overall specific rates of reaction of the immobilised biomass (Atkinson et al., 1981).

Khan et al. (1982) observed that, granular activated carbon packed anaerobic filter, when used for substrates like glucose and phenol resulted in better COD conversion, higher rates of methane production and lower biomass production. Anthracite coal packed filter did not show much improvement. McConville and Maier (1978) conducted a study to improve the performance stability and the rate of decomposition of anaerobic digesters by adding high surface area, powdered activated carbon (PAC). They evaluated the effects of small doses of activated carbon on the rates of methane generation, on the extent of decomposition of organic solids and on the stability of the process in terms of pH control at different detention times. The enhancement of methane was observed only 12 percent when PAC dose was 150 mg/l at detention times of 15.2, 7.6 and 4.0 days. They also observed

Table 2.2. Types of Reactor*

Type of reactor	Synonyms	Abbreviations	Commercial name (Company)
A) Non attached biomass			
1) Recycled flocs	Contact Process	-	Bioenergy process
2) Sludge blanket	Upflow Anaero-	UASB	Anamet process Biothan (Esmill UASB (CSM)
3) Digester			
B) Attached Biomass			
4) Fixed bed	Fixed film/ filter, Submerged Filter Stationary Fixed Film	SMAR/ANFIL (upflow) AUF (upflow) ADFR (downflow)/AF	Anflow
5) Moving bed	Rotating discs Rotating Biological Contactor	An RBC RBC	(Autotrol)
6) Expanded bed**	Anaerobic Attached Film Expanded Bed	AAFEB	Anitron process (Door-Oliver)
7) Fluidized bed**		FBBR	Hy-flow (Escolotrol)
8) Recycled bed	Carrier Assisted Contact Process	CASBER	

* After Harremoes and Henze (1982).

** Expanded bed and fluidized bed reactors work on the same basic principle. The only difference is that in fluidized beds, the percent expansion and recirculation ratio are higher (Harremoes and Henze, 1982; vanden Berg and Kennedy, 1983).

that PAC addition reduced the VSS at this dose and stabilization was improved. It was concluded by them that addition of PAC was not having any effect on bacterial growth rate coefficients of acid formers and the methane formers.

vanden Berg et al. (1981) reported that methane production rates of anaerobic fixed film fermentors using fired potters clay for film support (surface to volume ratio 110-140 m^2/m^3) exceeded those of anaerobic contact and fully mixed continuous fermenters both with simulated sewage sludge and with beam blanching waste as substrates. With the former waste maximum rates of methane production by the fixed film and contact process fermenters were 3.3 and 2.4 m^3 CH_4 (STP)/m^3/day, respectively. Using beam blanching waste maximum rates for the contact process were 1.5-2.0 m^3 CH_4 (STP)/m^3/day, while fixed film fermenter produced as much as 5.7 m^3/m^2/day. Additional advantages of fixed film over contact fermenters has been reported as elimination of mechanical mixing and sludge settling and return. Carrondo et al. (1983) while treating high strength acidic molasses fermentation wastewater by anaerobic filters (without sludge recycle) reported gas production to be 4.8 m^3/m^3/day, the methane content was found to be less than 40 percent. COD removal was observed to be 57 to 79 percent. Hickey and Owens (1981),used the anaerobic biological fluidized-bed process and showed it to be effective for the simultaneous generation of methane gas and stabilization of high-strength wastewaters. The results demonstrated that while treating wastes from, dairy, chemical and food processing industries

more than 80 percent BOD reduction was achieved with 92 percent of methane recovery of theoretically estimated value. Sand as fine grained media was used to provide large surface areas for the growth of biomass in the fluidized bed. It was concluded that long sludge retention times can be maintained for a short hydraulic retention times. It was analysed that the system is a net energy producer and it can payback on the initial capital expenditure in less than five years.

2.4. The Process Kinetics

To achieve the high efficiencies, in anaerobic systems, if the biological wastewater treatment process is carried out under controlled conditions, within specific boundaries, such a system can be termed as reactor. Changes in the composition and concentration of materials that occur while the wastewater is retained in the reactor are important factors in wastewater treatment. These changes are caused by hydraulic transport of materials into and out of the reactor as well as by reactions that occur within the reactor. To fully define a reactor system and design similar ones, it is necessary to know the rate at which the changes occur and the extent of the changes (Benfield et al., 1980).

Despite its many advantages, the anaerobic digestion has not yet reached its full potential, because of; (1) variable performance and operation, (2) lack of knowledge about the physical chemical and biochemical interactions, (3) use of empirical design procedures not firmly based on fundamental characteristics and process kinetics of the digestion system. A trouble free digester, which is subjected to a

design and control, without a sound knowledge of the process kinetics will merely be a chance.

From the kinetic viewpoint, anaerobic treatment may be described as a three step process involving (a) hydrolysis of complex material, (b) acid production and (c) methane fermentation. In such a complex multistep process, the slowest step will govern the overall kinetics of waste stabilisation. This slowest or rate limiting step in anaerobic treatment is the third-step, that is, methane fermentation (Lawrence et al., 1969; Cohen et al., 1979; Benefield et al., 1980).

Monod (1947) has described the relationship between the residual concentration of the growth-limiting nutrient and the bacterial growth rate by the equation

$$\mu = \mu_m \frac{S}{K_s + S} \qquad 2.4.1$$

where,

μ = specific growth rate of biomass, time^{-1}, which can be defined as $\frac{(dx/dt)}{x}$, where x is the concentration of biomass present

μ_m = maximum value of μ at saturation concentration of growth-limiting substrate, time^{-1}

S = residual growth-limiting substrate concentration, mass volume^{-1}

K_s = saturation constant numerically equal to the substrate concentration at which $\mu = \mu_m/2$, mass volume^{-1}.

Lawrence and McCarty (1969) relate the rate of substrate utilisation to the concentration of microorganism in the

reactor and to the concentration of substrate surrounding the organism by the equation

$$\left(\frac{ds}{dt}\right) = \frac{kxS}{K_s + S} \qquad 2.4.2$$

where,

$\left(\frac{ds}{dt}\right)$ = overall substrate utilisation rate, mass volume^{-1} time^{-1}

k = maximum specific substrate utilisation rate, time^{-1}

S = substrate concentration surrounding the biomass, mass volume^{-1}

K_s = saturation constant, which has a value equal to the substrate concentration when $(ds/dt)/x = k/2$, mass volume^{-1}

x = active biomass concentration, mass volume^{-1}.

Equation 2.4.2 can be written as

$$q = \frac{kS}{K_s + S} \qquad 2.4.3$$

where,

q = specific substrate utilisation rate, time^{-1}, which can be defined as $\frac{(ds/dt)}{x}$.

Growth yield, Y, is defined mathematically as

$$\frac{dx}{ds} = Y \qquad 2.4.4$$

This also can be written as

$$\frac{dx}{ds} = \frac{(dx/dt)/x}{(ds/dt)/x}$$

Therefore,

$$Y = \frac{\mu}{q} \qquad 2.4.5$$

Again, an expression which can be used to describe the net growth rate of microorganism in a completely mixed continuous anaerobic treatment system can be written as follows (Lawrence and McCarty, 1969)

$$\mu = Y q - K_d \qquad 2.4.6$$

where,

K_d = microorganism decay coefficient, time^{-1}.

Combining equations 2.4.3 and 2.4.6

$$\mu = Y \frac{kS}{K_s + S} - K_d \qquad 2.4.7$$

Lawrence and McCarty (1970) introduce an operational parameter called biological solids retention time (BSRT) symbolised by θ_c which is defined as the average time a unit of biomass remains in the treatment system.

Considering the material balance equation for biomass in a reactor, it can be obtained as

$$\mu = \frac{1}{\theta_c} \qquad 2.4.8$$

and also

$$\mu_m = \frac{1}{\theta_c^m} \qquad 2.4.9$$

where

θ_c^m = the minimum biological solids retention time, the BSRT at which biomass is removed from the system faster than it is produced.

For a reactor without biomass recycle, BSRT and hydraulic retention time are same, i.e. $\theta_c = \theta$.

Process failure due to kinetic stress will occur when the BSRT (θ_c) is reduced to θ_c^m. Under this condition waste treatment efficiency drop to zero and the effluent waste concentration, S, is equal to the influent waste concentration S_o. When S_o is large enough to be non-growth-limiting, the value of θ_c at which failure occurs is a characteristic of the waste as well as waste assimilating microbial population. In such case $S_o \simeq K_s + S_o$ and thus equation 2.4.7 reduces to the following approximate form which can be used to calculate the minimum value of BSRT (θ_c^m)

$$\mu_m = \frac{1}{\theta_c^m} = Y k - K_d \qquad 2.4.10$$

Grasius (1983) in an approach to formulate the kinetics of overall treatment system of anaerobic digestion, studied the kinetics of methane fermentation of a complex substrate (molasses) and simple substrate glucose. He used semi-continuous fed reactor without stirring. The digesters were subjected to a programme of steady state operation at several different HRT and the system parameters were measured. The fermentation temperature used was 37°C. Lawrence and McCarty (1969) also evaluated the parameters for organic acids in a continuous stirred reactor. McConville and Maier (1978) gave the kinetic parameters data for sludge of municipal wastewater treatment plant based on the data of Metcalf and Eddy (1972) for a system in which PAC was added to provide additional surface area for growth of microorganism. The results are summarised in Table 2.3.

Table 2.3. Values of Kinetics Constants Obtained for Different Substrates

Type of substrate	k day^{-1}	K_s mg/l	μ_{max} day^{-1}	Y	K_d day^{-1}	Sources of data
Molasses	-	1590	0.39	0.045	0.029	Grasius (1983)
Glucose	-	1558	0.49	0.052	0.02	-do-
Acetic acid	8.1	154	0.36	0.04-0.054*	0.01-0.04*	Lawrence and McCarty (1969)
Propionic acid	9.6	32	0.285	0.04-0.054*	0.01-0.04*	-do-
Butyric acid	15.6	5	0.238	0.04-0.054*	0.01-0.04*	-do-
Sludge	-	500	0.4	0.05	0.01	McConville and Maier (1978)

* Range in fermentation of volatile acids.

The food/microorganism (F:M) ratio has been considered as design criterion for organic loading and is defined as the substrate load applied to the process per unit of biomass in the tank per unit time (Benefield, 1980). Hence, the F:M ratio can be expressed mathematically as

$$F:M = \frac{Q S_o}{XV} \qquad 2.4.11$$

where,

S_o = the influent substrate concentration, mass $volume^{-1}$

V = the volume of the reactor, volume

Q = the rate of raw wastewater flowing to the tank, $volume\ time^{-1}$.

An equation can be developed relating F:M ratio to θ_c by taking a material balance for substrate entering and leaving the reactor at steady state as

$$\frac{1}{\theta_c} = Y_T \cdot \frac{Q(S_o - S_e)}{XV} - K_d \qquad 2.4.12$$

where S_e = substrate concentration in the effluents, mass volume^{-1}.

Substituting for $\frac{Q\ S_o}{XV}$ from equation 2.4.11 then gives

$$\frac{1}{\theta_c} = Y_T\ (F:M - \frac{Q\ S_e}{XV}) - K_d \qquad 2.4.13$$

Since the QS_e/XV term is normally very small compared to the value for the F:M ratio, equation 2.4.13 can be approximated as

$$\frac{1}{\theta_c} \simeq Y_T\ (F:M) - K_d \qquad 2.4.14$$

In equation 2.4.14, knowing the influent substrate concentration and using the Y_T (same as Y) and K_d values for the type of substrate it is possible to determine the biomass concentration.

Chen and Hoshimoto (1978) have taken entirely a different approach to explain the process kinetics of biomethanation. They refer to the final product of digestion process, i.e., the methane gas and, a kinetic model describing the methane fermentation rate as a function of waste biodegradability, loading rate, and detention time for a continuous, completely mixed fermentation system without solids recycle was proposed

$$B = B_o \left(1 - \frac{K_H}{\mu_m \theta - 1 + K_H}\right) \qquad 2.4.15$$

or

$$G_s = \frac{B_o S_o}{\theta} \left(1 - \frac{K_H}{\mu_m \theta - 1 + K_H}\right) \qquad 2.4.16$$

where,

B = methane yield, volume CH_4 mass^{-1} COD added

G_s = volumetric methane yield, volume CH_4 volume^{-1} fermenter time^{-1}

B_o = ultimate methane yield, volume CH_4 mass^{-1} COD added as $\theta \rightarrow \infty$

S_o = influent total COD, mass volume^{-1}

θ = retention time, time

μ_m = maximum specific growth rate of microorganism, time^{-1}

K_H = kinetic parameter, dimensionless.

The maximum volumetric methane production rate, G_{max}, was obtained by taking the derivative of G_s with respect to θ and equating it to zero. So,

$$G_{max} = B_o S_o \mu_m / (1 + \sqrt{K_H})^2 \qquad 2.4.17$$

which occurs at a detention time, θ_{Gmax}

$$\theta_{Gmax} = (1 + \sqrt{K_H})/\mu_m \qquad 2.4.18$$

Chen et al. (1980) studied the effect of temperature on methane fermentation kinetics of beef-cattle manure. In semi-continuous systems, plotting the steady state methane yield (liter CH_4/g VS added) versus the reciprocal of θ and

extrapolating to an infinite θ (i.e., as $\frac{1}{\theta} \rightarrow 0$), the ultimate methane yield (B_o) were found out using equation 2.4.15 with a non-linear least-square fit of experimental data, they found the value of μ_m and K_H, and by substituting the values of B_o, K_H, and μ_m, for known value of S_o, they calculated G_{max} and θ_{Gmax}. Chen and Hashimoto (1978) calculated the μ_{max} values for different loading of a sludge based on gas data of dairy waste and beef waste. The μ_{max} values for dairy waste (influent VS concentration of 60 to 140 g/l) was found to be 0.79 day^{-1} while that for beef waste (influent VS concentration of 57 to 117 g/l) is 0.77 day^{-1}. The calculations of μ_{max} and K_H were based on the method as mentioned earlier. From the results it is observed that at a particular temperature the μ_{max} value do not vary with increase in loading rates, whereas the K_H values have been found to be varying.

However, when the data (Varel, 1977) of VFA production was plotted as function of HRT (θ) linearity was not observed and hence it was not possible to calculate μ_{max} value. The gas data instead of VFA data can be used for the calculation of μ_{max} as it was found to follow the linear trend.

It is important to note that the kinetic parameters K_H is a function of the influent substrate concentration and type of substrate. Hence, evaluation of K_H and other parameters for different wastewaters are essential for designing a treatment system which also produces maximum gas.

3. NEED FOR PRESENT STUDY

Anaerobic digestion has a long history of use. The slow rate of digestion and poor stability of the systems are known facts in spite of its wide use in the waste treatment system. As mentioned in literature, efforts have been made for improving the performance stability and the rate of decomposition in anaerobic digesters by adding high surface area. Activated carbon in powdered as well as granular forms besides flyash and coal have been used. However information regarding the kinetic parameters like μ_{max}, K_s, Y and K_d for digesters receiving additives, treating complex wastes is scanty. Since activated carbon is a costly material to be used for waste treatment, it is appropriate that an investigation should be carried out for increasing methane production by using low cost additives like coal and coconut shell powder as fine additives and cinder, rashing rings as coarse additives. Presence of additives allows further increase in organic loading of the digester which reduces the volume of the reactors. This investigation is also directed to evaluate the digesters performance at very high organic loading rates. It is also felt necessary to determine kinetic parameters for a more realistic design of digesters when additional surface area for the growth of microbes is provided in the system.

4. EXPERIMENTAL METHODOLOGY

Experimental methodology is broadly classified into two categories, namely, methods of study and analytical techniques.

4.1. Method of Study

The present investigation is induced to evaluate the enhancement of gas production by additives. Bituminous coal powder (BCP) and coconut shell powder (CSP) passing 85 micron sieve were respectively fed at a rate of 2500 mg/l to two digesters alongwith the daily feed. Another digester was maintained without any of these additives to serve as control. The digesters containing cinder and RR were fed with substrate represented as attached growth systems. Glucose as a simple substrate and molasses as an industrially produced complex substrate have been employed in the investigation. The semicontinuous feeding system was employed for the digesters. In first phase of investigation hydraulic detention time of digesters was kept constant and the organic loading in terms of Kg of COD/m^3/day was increased to determine the resultant gas production and effluent quality. In second phase of investigation different hydraulic detention times were employed for producing gas and determining the kinetic parameters for process design.

4.1.1. Composition of Feed

Molasses was collected from the small sugar industry of National Sugar Institute, Kanpur. It was diluted

COD, for loading the digesters. The average chemical composition of the molasses is given in Table 4.1. In order to supplement the nutrient a synthetic media containing nitrogen, phosphorus and other trace elements as given in Table 4.2 (Kroker et al., 1979) was used. The daily feed used to be prepared for all the digesters togather to ensure the same influent. Bituminous coal powder (BCP) and coconut shell powder (CSP) was added on the basis of 2500 mg/l of digester volume. The quantity of BCP and CSP were added in the daily feed depending upon the quantity of influent required to be fed on that particular day. The effluents are withdrawn from the digesters daily after vigorous shaking, such that BCP or CSP also are withdrawn. Coal or coconut powder are daily added alongwith the feed. This allows to maintain same HRT.for the additives. In case of cinder and RR digesters only daily feed was added and the effluent was withdrawn. The seed for the molasses and glucose digesters for this study was taken from digesters fed respectively with molasses and glucose and maintained at 8/6 days hydraulic detention time, fed with 20 g/l of organic COD load on daily basis.

4.1.2. Experimental Set-Up

Two liter glass aspirator bottles with necessary inlet, outlet and off gas collection arrangements were used to serve as the digesters. These bottles were placed in a constant temperature water bath maintained at 35 $\pm$ 2°C. The gas production was measured using liquid displacement of standard sodium chloride solution containing 5 percent by volume of H_2SO_4 and methyl orange.

Table 4.1. Average Characteristics of Feed Molasses (100 g/l)

Parameter	Concentration, mg/l, except for pH
pH	5.0-6.5
COD	76×10^3
BOD	60.8×10^3
Total nitrogen as N	0.4×10^3
Potassium as K	2.25×10^3
Calcium as Ca	1.06×10^3
Total carbohydrate as glucose	43.63×10^3
Reducing sugar as glucose	11.6×10^3
Sulphate as SO_4	1.39×10^3
Volatile solids (VS)	57.3×10^3
Fixed solids (FS)	6.55×10^3

Table 4.2. Synthetic Media Composition* (Kroeker et al., 1979)

Compound	Concentration, mg/l
KH_2PO_4	4000
$MgSO_4.7H_2O$	126
$CoCl_2.6H_2O$	36
$FeCl_3.6H_2O$	864
$CaCl_2.6H_2O$	600
Urea	4000
Yeast extract	400

4.1.3. Loading Schedule

Using glucose and molasses as the substrates, two sets of five digesters each were run with varying influent COD load (S_o) of 20 g/l as glucose and 20 g/l COD load as molasses. The detention time (θ) was kept constant as 6 days in the first phase of studies. After the digesters has attained steady state, volatile fatty acids, gas production and COD removal were determined. Subsequently the digesters were subjected to a higher organic loading, and after the digesters have attained steady state (which requires approximately 2 to 3 hydraulic turnovers), the above parameters have been determined consequtively for three days to obtain data at that loading. This process continued for loadings to obtain the data. In the second phase of studies, two sets of digester were run, having five digesters in each, with influent loads (S_o) 20 g/l as glucose, and 20 g/l COD for molasses. Keeping the organic load constant the digesters were maintained at different hydraulic retention times (HRTs) and at each HRT after the digesters had attained steady state, volatile fatty acid concentration, gas production and COD removal were determined. The schedule of digesters feeding in both phases alongwith pertinent in formation are presented in Tables 4.3 and 4.4.

The digesters were operated as semi-continuous systems. After thoroughly shaking the digesters, a definite quantity of mixed liquor depending upon the hydraulic detention time was withdrawn every day and, immediately replacing it with equal quantity of solution containing the daily feed, fine

(HRT Remains Constant)

Type of substrate	Influent substrate concentration (S_o) g/l	Loading rate for detention time of 6 days, $Kg/m^3/day$				
		Digester with no surface (control)	Digester with bituminous coal powder (BCP)	Digester with coconut shell powder (CSP)	Digester with cinder as coarse surface	Digester with rashing ring as coarse surface
Glucose	20	3.33	3.33	3.33	3.33	3.33
	25	4.166	4.166	4.166	4.166	4.166
	30	5.00	5.00	5.00	5.00	5.00
Molasses	20	3.33	3.33	3.33	3.33	3.33
	25	4.166	4.166	4.166	4.166	4.166
	30	5.00	5.00	5.00	5.00	5.00
	35	5.83	5.83	5.83	5.83	5.83
	45	7.5	7.5	7.5	7.5	7.5
	55	9.166	9.166	9.166	9.166	9.166
	65	10.83	10.83	10.83	10.83	10.83
	75	-	-	-	12.50	12.50
	85	-	-	-	14.166	14.166

The rate of addition of BCP and CSP alongwith the influent is 0.416 $Kg/m^3/day$.

(Influent Substrate Concentration (S_o) Remains Constant)

Type of surface added/ available	Loading rate (molasses/glucose) for the indicated detention time (days)@, Kg/m^3/day								Quantity of surface added for the indicated detention time (days)*, Kg/m^3/day					
	8	6	4	2.67	2.0	1.6	1.33	1.0	8	6	4	2.67	2.0	1.33
No surface (control)	2.5	3.33	5.0	7.5	10.0	-	15.38	-	-	-	-	-	-	-
Bituminous coal powder	2.5	3.33	5.0	7.5	10.0	-	15.38	20	0.3125	0.416	0.625	0.936	1.25	1.88
Coconut shell powder	2.5	3.33	5.0	7.5	10.0	-	15.38	20	0.3125	0.416	0.625	0.936	1.25	1.88
Rashing rings	-	3.33	5.0	7.5	10.0	12.5	15.38	20	-	-	-	-	-	-
Cinder	-	3.33	5.0	7.5	10.0	12.5	15.38	20	-	-	-	-	-	-
No surface control)	2.5	3.33	5.0	7.5	-	-	-	-	-	-	-	-	-	-
Bituminous coal powder	2.5	3.33	5.0	7.5	-	-	-	-	0.3125	0.416	0.625	0.936	-	-
Coconut shell owder	2.5	3.33	5.0	7.5	-	-	-	-	0.3125	0.416	0.625	0.936	-	-
ashing rings	-	3.33	5.0	7.5	10.0	12.5	15.38	20	-	-	-	-	-	-
inder	-	3.33	5.0	7.5	10.0	12.5	15.38	20	-	-	-	-	-	-

Influent substrate concentration S_o = 20 g/l on COD basis for molasses and glucose.

Rashing rings and cinder were added 1.5 liter for 1.5 liter of digester fluid respectively.

additives, nutrient media and required quantity of sodium bicarbonate buffers to maintain a mixed liquor pH around 7.2-7.8.

After the digesters had been maintained at the designated θ for two volume turnovers to ensure steady state, two/three daily sampling were obtained and analysed for pH, volatile fatty acid (VFA), bicarbonate alkalinity, inorganic phosphate, COD, and reducing sugar. Besides monitoring the total gas production, the methane content of the gas was assessed by allowing it to pass through a KOH trap (six normal). Kinetics of gas production for total gas and methane for a period of 24 hrs were taken during the steady state studies.

4.1.4. Revival of Digesters

In treatability studies, when digesters fed with molasses reached at a levels of 13000-14000 mg/l of VFA, it was observed that methane content reduced to a extent of 10 to 20 percent and COD removal rate went down to 22 to 29 percent. At this level revival of digester was carried out.

Revival was carried out in molasses fed digesters by starvation and the increase in pH by addition of alkali (lime). The pH of the system was raised to 8.3 to 8.5 to reduce the unionised fraction of VFA, which is considered to be more toxic. Digesters were allowed to starve till the levels of VFA come down to a original level at approximately 4.16 Kg COD/m^3/day. The feeding of the digesters was again started at this point till the steady state conditions were achieved. The effluent of digesters were analysed

for VFA, total gas and methane. The rate of organic loading subsequently increased and at the steady state conditions the above mentioned parameters were determined.

Revival of glucose fed digester was tried by raising the pH only through addition of lime, which did not help in reviving the digesters.

4.2. Analytical Techniques

Samples for analysis were taken from the wasted mixed liquor. The pH of this sample was measured and for the determination of VFA, bicarbonate alkalinity, inorganic phosphate, total carbohydrate, and COD, the supernatant after its centrifugation (Sorvall, SS-3, Automatic superspeed centrifuge) was used. The various analytical methods used in this study are given below.

4.2.1. pH

pH was directly measured using a pH meter (Systronics, Model 331, India).

4.2.2. VFA and Bicarbonate Alkalinity

Direct titration method given by Delallo et al. (1961) was modified for phosphate interference. This was used to determine the VFA and bicarbonate alkalinity.

(i) Theory: The direct method involves titration of sample with strong acid to pH 4.5, which gives alkalinity due to HCO_3^-, VFA and also other ions like phosphate. When the sample pH is reduced to 3.3, HCO_3^- will be converted to carbonic acid and subsequent boiling of the sample removes all the carbonic acid and carbon dioxide remaining in the solution. The

back titration from pH 4 to 7 will measure the alkalinity due to organic acids and other minor ions present. The conversion factor for determination of VFA from volatile acid alkalinity depends on the proportion of acid which is titrated between pH 4 to 7.

(ii) Procedure: 25 ml of the centrifuged sample was taken and was titrated to a pH 4.5 with 0.1 N H_2SO_4. The acid used was noted and continued the addition of acid to pH 3.5-3.3. The sample was then gently boiled for 3 minutes on the reflexing apparatus and cooled in a water bath to room temperature. It was then titrated against 0.05 N NaOH upto a pH 4.0. After noting the burette reading, the titration was continued to pH 7.0 and final reading was noted. VFA concentration was calculated as follows:

VFA alkalinity, mg/l as $CaCO_3$

$$= \frac{\text{ml 0.05 N NaOH} \times 2500}{\text{ml of sample}} \qquad 4.1$$

VFA, mg/l as CH_3COOH

$$= \text{VFA alkalinity, mg/l as } CaCO_3 \times 1.5 \qquad 4.2$$

The multiplying factor 1.5 takes care of the conversion of $CaCO_3$ alkalinity to VFA expressed in terms of CH_3COOH and the assumption that 80 percent of VFA is titrated from pH 4.0 to 7.0. The bicarbonate alkalinity was obtained as follows:

Total alkalinity, mg/l as $CaCO_3$

$$= \frac{\text{ml } 0.1 \text{ N } H_2SO_4 \text{ (used upto pH 4.5)} \times 5000}{\text{ml sample}} \qquad 4.3$$

Bicarbonate alkalinity, mg/l as $CaCO_3$

$$= \text{Total alkalinity} - \text{VFA alkalinity} \qquad 4.4$$

(iii) Correction for Phosphate: DeLallo et al. (1961) reports that the back titration from pH 4 to 7 includes the organic acid and other ions, mainly phosphate. The contribution of phosphate ions in samples with low concentrations of VFA will be more critical. So a correction to eliminate the phosphate interference was applied as reported by (Gracius, 1983).

The inorganic phosphate content (P_o) of the nutrient medium solution was found using the method given later in this chapter. 25 ml of medium was taken and titrated as explained earlier, and ml of NaOH used from pH 4 to 7 was noted. This quantity represented the alkalinity due to phosphate only, because the medium did not contain any VFA. From this phosphate correction was obtained as follows:

Phosphate alkalinity titratable from pH 4-7,

$$\text{mg/l as } CaCO_3 \ (P_t) = \frac{\text{ml } 0.05 \text{ N NaOH} \times 2500}{\text{ml medium}} \qquad 4.5$$

Percentage of phosphate titratable from pH 4-7,

$$P = \frac{P_t}{P_o} \times 100 \qquad 4.6$$

The same percentage of titratable phosphate was applied to the sample to eliminate the phosphate interference. If the phosphate content of the digester effluent is P_d

The phosphate alkalinity correction, mg/l as $CaCO_3$

$$= P \times P_d \qquad 4.7$$

Corrected VFA alkalinity, mg/l as $CaCO_3$

$$= \text{VFA alkalinity} - P \times P_d \qquad 4.8$$

From this corrected VFA alkalinity the VFA concentration was calculated using Eq. 4.2.

(iv) Determination of Inorganic Phosphate: The analysis of inorganic phosphate was required with determination of VFA. Inorganic phosphate was assayed according to the modified method of Tausaky and Shorr (Warton and McCarty, 1972). Inorganic phosphate reacts with ammonium molybdate under acidic pH conditions to form phosphomolybdic acid. This is reduced to phosphomolybdous acid by ferrous sulphate. Phosphomolybdous acid, thus, formed has an intense blue colour with absorption maxima at 660 nm.

Reagents:

a. Colour Reagent: 4 ml of 10 percent ammonium molybdate in 10 N H_2SO_4 was added to 36 ml distilled water in which 2 g of $FeSO_4$ was added. This reagent was prepared fresh every time.

b. Standard Phosphate Solution: 136 mg of potassium dihydrogen phosphate (KH_2PO_4) was dissolved in 100 ml distilled water. 1 ml of this solution diluted 10 times yields a concentration of 1 µmol (136 µg) of phosphate.

c. Trichloroacetic Acid: 10 g TCA was dissolved in 100 ml distilled ater so as to yield 10 percent TCA.

To 1 ml of aliquot, 1 ml of 10 percent TCA was added. After thorough mixing, 1 ml of colour reagent was added and allowed to stand for 10 minutes for the colour development. The volume was made to 5 ml and the optical density (OD) was measured at 660 nm against a reagent blank. A calibration curve, using phosphate standards was prepared according to the above method.

4.2.3. Chemical Oxygen Demand (COD)

COD analysis was conducted as per the Standard Methods (1976).

4.2.4. Reducing Sugar

Arsinomolybolid acid reagent was used to determine the reducing sugar content of the digester effluent (Somogyi, 1952).

(i) Theory: Cupric ions are reduced to cuprous ions in the presence of reducing sugars. The amount of cuprous ions formed is determined by adding arsenomolybdate reagent. Arsenomolybdic acid is reduced to arsenomolybdous acid by cuprous ion. The blue

colour of arsenomolybdous acid is measured colourimetrically.

(ii) Reagents:

a. Tartarate Solution: 12.5 g of Na_2CO_3, 12.5 g of rochelle salt and 10 g of $NaHCO_3$ were weighed and 400 ml distilled water was added to it. After adding 100 g of Na_2SO_4 to the solution, it was diluted to 500 ml.

b. $CuSO_4$ Solution: 15 g of $CuSO_4$ was dissolved in 100 ml distilled water and 1 or 2 drops H_2SO_4 was added.

c. Arsenomolybdate Reagent: 25 g ammonium molybdate was dissolved in 450 ml distilled waters and 21 ml concentrated sulfuric acid was added while stirring. 3 g sodium arsenate dissolved in 25 ml water was added to ammonium molybdate solution with stirring. This solution was placed in a incubator at 37°C for 24 hours and then stored in a brown bottle.

d. Stock Glucose Solution: 0.1 percent solution of glucose was prepared in a saturated solution of benzoic acid. Working standard was prepared by diluting the stock solution ten times.

(iii) Procedure: Sugar standards containing 0-100 g were taken in different test tubes and the volume made upto 1 ml. Tartarate-$CuSO_4$ reagent was prepared freshly for each analysis by adding 2 ml of $CuSO_4$ solution to 50 ml of tartarate solution. One ml of this reagent was added to the above test tubes and kept in a boiling

water bath for 15 minutes. After cooling the tube, 1 ml of arsenomolybdate reagent was added and after a minute the content was diluted to 10 ml. The optical density was measured at 510 nm. The above procedure was followed for the samples from the digesters.

4.2.5. Nitrogen-Total

In order to decide the quantity of nitrogen to be supplemented to the digesters when molasses was used as substrate, the total nitrogen already present in the molasses was determined by the method given by Thompson et al. (1951). In a 100 ml Kjeldal flask, 10 ml of the sample (containing 5-200 µg of nitrogen) was taken to which 4 ml of 3 N sulfuric acid was added. Glass beads were added to avoid bumping, and digestion was carried out for 10 minutes after the white fumes started appearing. After cooling, contents of the Kjeldal flask were transferred to a 50 ml beaker and the pH was adjusted to about 7.0 with 1.25 N NaOH. Total volume was made upto 25 ml in a standard volume flask and 10 ml or aliquot diluted to 10 ml was taken for Nesslerisation. Nesslerisation was done as given in Standard Methods (1976).

4.2.6. Calcium

To characterise the molasses with respect to calcium, it was determined by the EDTA titrimetric method as given in Standard Methods (1976).

4.2.7. Sulfate

The sulfate present in the molasses was determined by the gravimetric method given in Standard Methods (1976).

4.2.8. Potash

A flame photometer (Model CL-22A, Elico Pvt. Ltd., India) was used to determine the potash content of the molasses. The analysis was carried out as per the method given in the instrument instruction manual.

4.2.9. Biochemical Oxygen Demand (BOD)

The effluent samples at steady-state conditions from different digesters were taken and centrifuged. The molasses and these samples were diluted with dilution water (on the basis of COD) to an extent that the expected depletion of DO is 2, 3 and 4 mg/l. Further analysis were conducted as per the procedure given in Standard Methods (1976).

5. RESULTS AND DISCUSSION

The objective of the investigation is to evaluate the effects of low cost powdered and granular additives on enhancement of gas production and improvement in effluent quality of anaerobic digesters. Further, determination of the behavioural parameters of the rate limiting group of organisms namely the 'methane formers' to facilitate the design of anaerobic digester loaded with different additives is also envisaged. The first part deals with the evaluation of kinetic parameters of methane formers in molasses and glucose fed digesters containing bituminous coal powder (BCP), coconut shell powder (CSP) as fine additives, rashing rings and cinder as coarse material which provide surface for growth. Second phase deals with gas production and effluent quality for molasses and glucose fed digesters with coarse and fine additives. The results are compared with those of digesters not receiving any surface (control digester).

5.1. Process Study

To obtain sufficient data for the evaluation of kinetic constants for the system using molasses and glucose as the substrates, digesters fed with different influent substrate concentrations were operated on semi-continuous basis without sludge recycle at different hydraulic retention times (HRT). The system parameters, viz., VFA, gas production and effluent COD were determined at steady state conditions. As sludge recycle was not adopted, the hydraulic detention time (HRT-θ) represented the biological solids

retention time (BSRT-Θ_c). Further, studies were also carried out with digesters containing RR and cinder which represent the attached growth systems. The BSRT values for these systems are expected to be different from HRT, and are evaluated by using maximum specific growth rate for suspended growth system (control digester). Discussion of these are presented in the following sections.

5.1.1. Evaluation of Kinetic Constants

The kinetic constants for methane fermentation were evaluated employing semi-continuous digesters without sludge recycle fed with molasses and glucose receiving bituminous coal powder (BCP), coconut shell powder (CSP). Control digester without additives were used to represent suspended growth system. Two different sets of digesters containing RR and cinder were also fed by molasses and glucose along with control digesters. The influent substrate concentration (S_o) of 20 g/l as COD for both molasses and glucose have been used for all digesters. These were subjected to a programme of steady state operation at several HRT as shown in Table 4.4. These system parameters were measured and the data are given in Appendices 1 and 2.

5.1.2. μ_{max} and K_s Determination

The kinetic constants μ_{max} and K_s were determined using the steady state effluent VFA, and COD values for different detention times as follows.

Taking reciprocal of both sides of equation 2.4.1 a linearised form as shown below is obtained:

$$\frac{1}{\mu} = \frac{K_s}{\mu_m} \cdot \frac{1}{S} + \frac{1}{\mu_m} \qquad 5.1$$

Considering equation 2.4.8, equation 5.1 can be written as

$$\theta = \theta_c = \frac{K_s}{\mu_m} \cdot \frac{1}{S} + \frac{1}{\mu_m} \qquad 5.2$$

5.1.2.1. μ_{max} and K_s Determination for Suspended Growth System

A plot of equation 5.2 using $\theta(\theta_c)$ and 1/S as variables, yielded the constants μ_m and K_s for control digesters (no surface). In case digesters with fine additives, as additives are added and withdrawn from the system daily alongwith feed and effluent, the HRT and BSRT can be assumed to be equal. Consequently μ_{max} and K_s have been evaluated similar to control digesters. These represents in system parameters for suspended growth systems. These constants for methane formers were obtained using the steady state effluent VFA, whereas by the substitution of COD values for S in equation 5.2 gave these values for the overall system. Figures 5.1 and 5.2 represent the plots of equation 5.2 using VFA values for 20 g/l molasses and glucose concentration for control BCP and CSP digesters. Similarly, μ_{max} and K_s values were obtained using COD values for S for molasses and glucose concentration of 20 g/l with and without additives. The reciprocal of μ_{max} gave the minimum biological retention time θ_c^m or θ^m. These values are summarised in Table 5.1 which is presented later on.

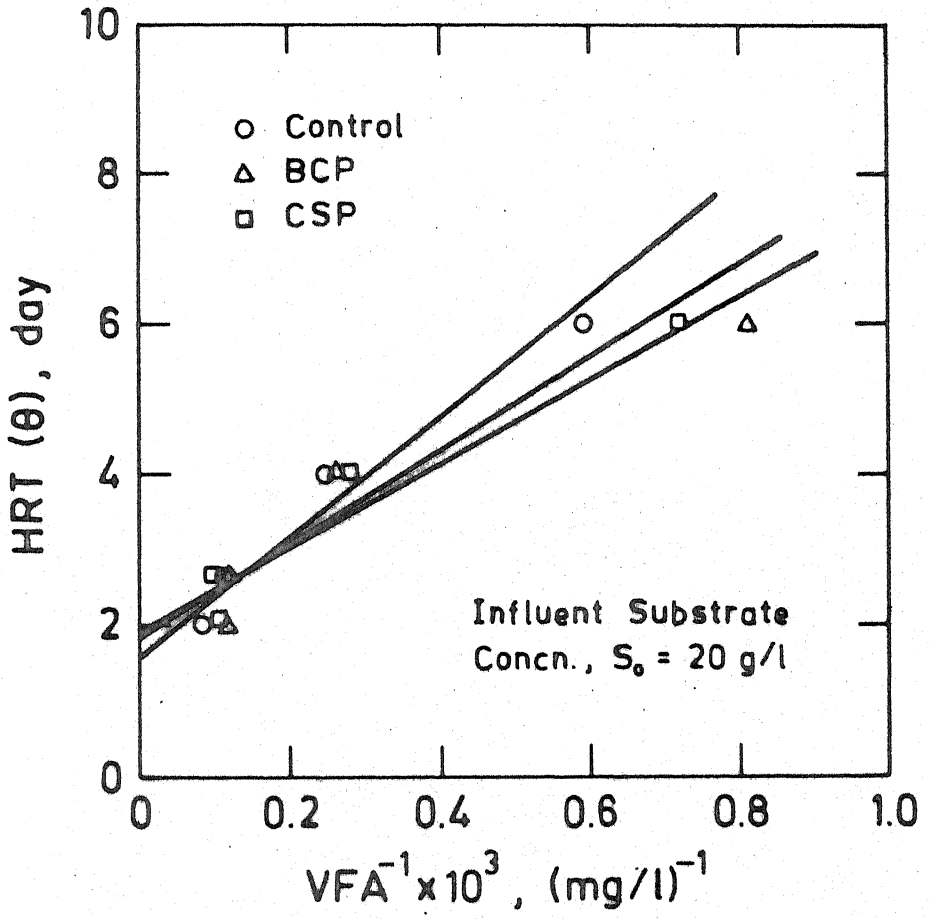

Fig. 5.1. Steady State Effluent VFA as a Function of Hydraulic Retention Time (HRT). Molasses as Substrate.

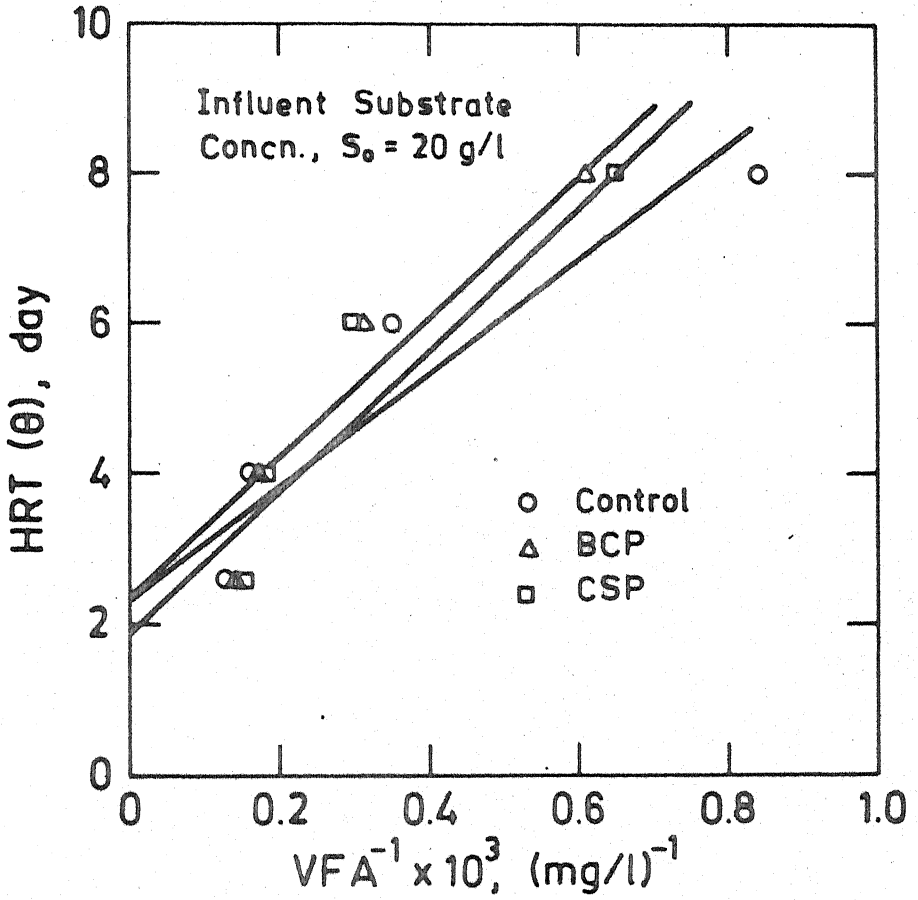

Fig. 5.2. Steady State Effluent VFA as a Function of Hydraulic Retention Time (HRT). Glucose as Substrate.

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5.1.2.2. μ_m and K_s Determination for Attached Growth System

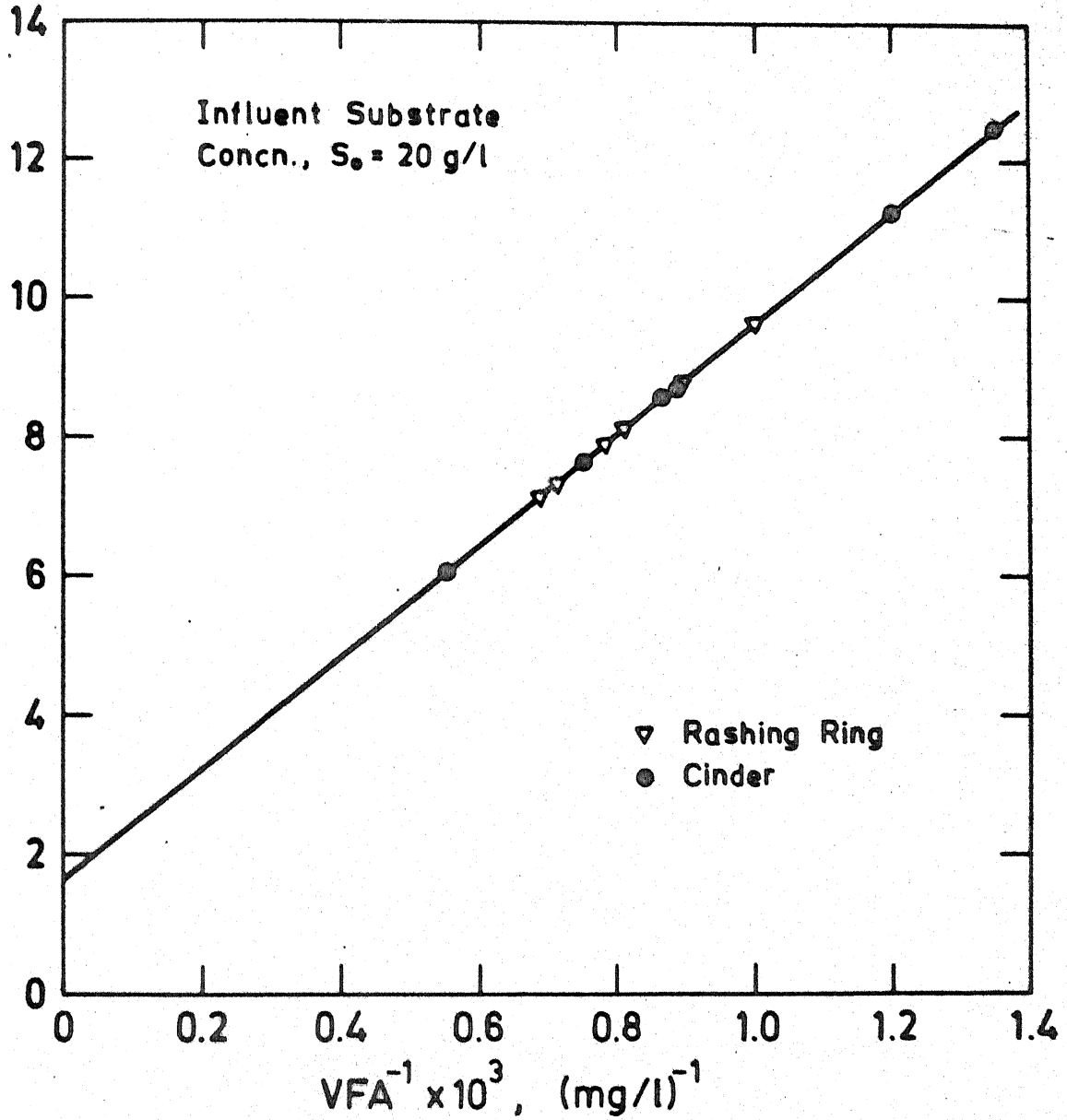
Attached microbial growth is expected in digesters containing RR and cinders, as on these, microbes get attached. Further, unlike in digesters with fine additives there was no daily withdrawal of these granular material. Due to this the HRT is expected to be different from BSRT though no sludge recycle was adopted. The BSRT for RR and cinder digesters fed with molasses and glucose are calculated as following. μ_{max} and K_s can be assumed to be constant for a given type of substrate whether the organisms grow on surface or otherwise. The specific growth rate (μ) for different HRT values for attached growth system have been calculated using μ_{max} and K_s for suspended growth digesters (control) and steady state VFA values of RR and cinder digesters. The BSRT (θ_c) values were then calculated for attached growth system by taking the reciprocal of above computed values. The plot to evaluate μ_{max} and K_s from computed θ_c values and VFA is presented in Figure 5.3 and the values are tabulated in Table 5.1.

5.1.3. Y and K_d Determination

Y and K_d for methane formers were evaluated using equation 2.4.6 in which μ and q are variables. To facilitate the calculation of q, equation 2.4.3 was used

$$q = \frac{kS}{K_s + S}$$

The maximum specific substrate utilisation rate, K, at the experimental temperature, 37°C has been taken as 10.38 day^{-1}



3. Steady State Effluent VFA as Function of Biological Solids Retention Time (BSRT). Molasses as Substrate.

(Grasius, 1983). This value of K was substituted in equation 2.4.3 alongwith already evaluated K_s value to calculate q for different VFA(s), subsequently a plot between q and μ ($\frac{1}{\theta}$) was prepared as per the following equation

$$\mu = Y q - K_d$$

The values evaluated from the linear plots for different additives are presented in Table 5.1.

5.1.4. B_o, μ_{max} and K_H Determination

Chen and Hashimoto (1978) have proposed a method of evaluating μ_{max} and K_H from easily measurable methane produced. In the following section these are determined for molasses and glucose fed digesters containing different additives as per the following procedure.

The quantity of methane produced was converted to that at NTP and was used to determine the methane yield (B), ml methane/g COD added or destroyed at steady state and volumetric methane yield (G_s), ml CH_4/l/digester day. As per Chen and Hashimoto (1978) B_o, the ultimate methane yield was obtained by a plot between B and $\frac{1}{\theta}$ or B and $\frac{1}{\theta_c}$ (attached growth) and extrapolating it to $\frac{1}{\theta} = 0$. From this, B_o values were evaluated for different systems. These values have been tabulated in Table 5.1.

Now rearranging the terms of equation 2.4.15 a linearised form of the same as shown below is obtained

$$\frac{B_o}{B_o - B} = \frac{\mu_m}{K_H} \cdot \theta + \frac{K_H - 1}{K_H} \qquad 5.3$$

Using the computed values of B_o for a particular substrate and its concentration, $B_o/(B_o - B)$ was calculated for different values of B corresponding to different θ. This was plotted against θ as shown in Figure 5.4 for molasses (20 g/l) yielding μ_m and K_H for fine surface additives and control. $\mu_{max.}$ and K_H values for other digesters (RR and cinder) have also been calculated in a similar fashion and the results are presented in Table 5.1.

Substituting the values of μ_m and K_H, in equation 2.4.17 for different values of S_o, $G_{max.}$ the maximum volumetric methane yield and $\theta_{Gmax.}$ the detention time to obtain this were calculated. These are also tabulated in Table 5.1. The experimental values as plotted in Figure 5.5 for molasses fed digesters containing fine additives and control, shows that the observed volumetric methane yield increases to a maximum with decrease in θ and further decrease in θ resulted in decrease of gas yield with the subsequent failure of system. It is evident from Figure 5.6 that similar trend in methane production is observed when it is against θ_c for RR and cinder digester.

5.1.5. Comparison of the Kinetic Constants

All the kinetic constants evaluated for the two substrates from different approaches namely the effluent VFA, COD and gas production, are presented in Table 5.1 for comparison.

The results obtained using VFA data pertain to the methanogens utilising acetate for their growth, whereas the constants from COD values reflect the digester's overall

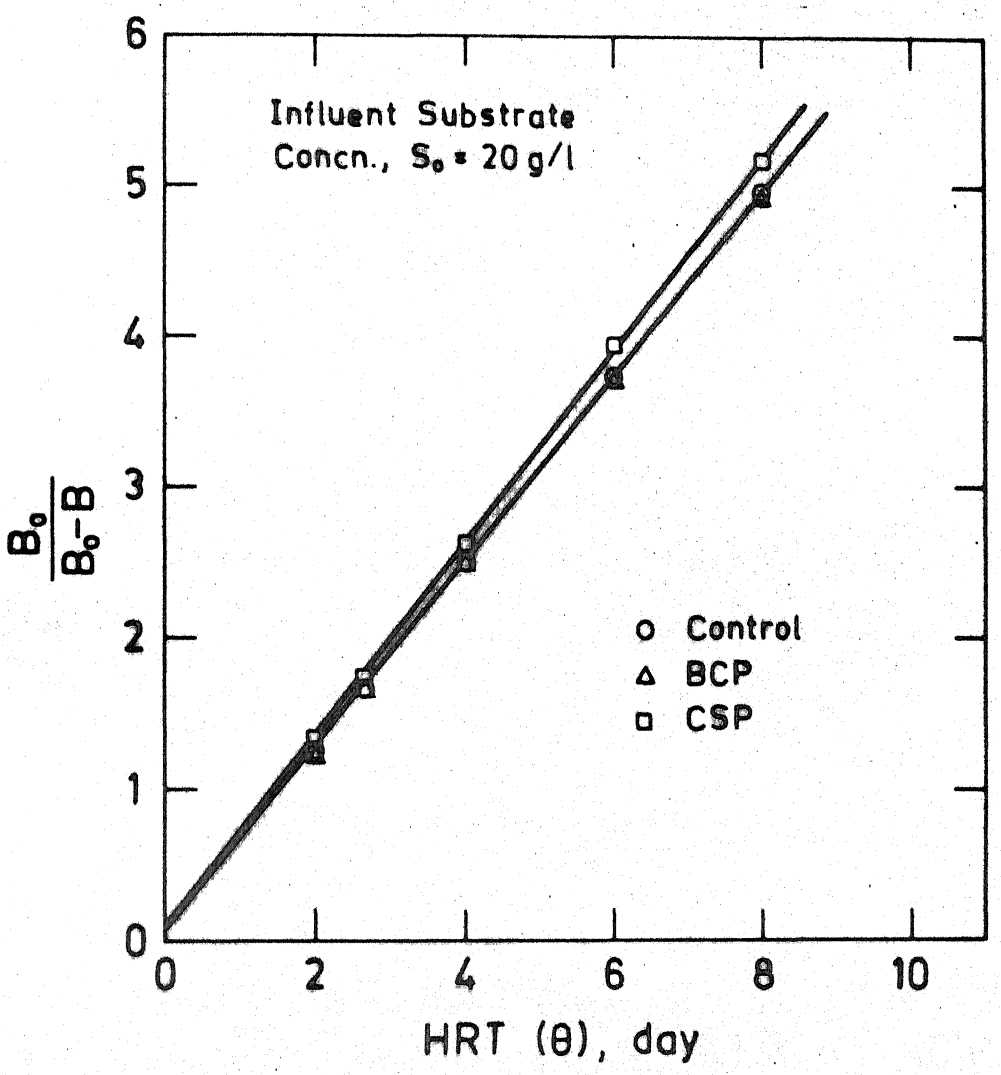


Fig. 5.4. Linearised Kinetic Model Relating Ultimate Methane Yield (B_o), Methane Yield (B) and HRT (θ).

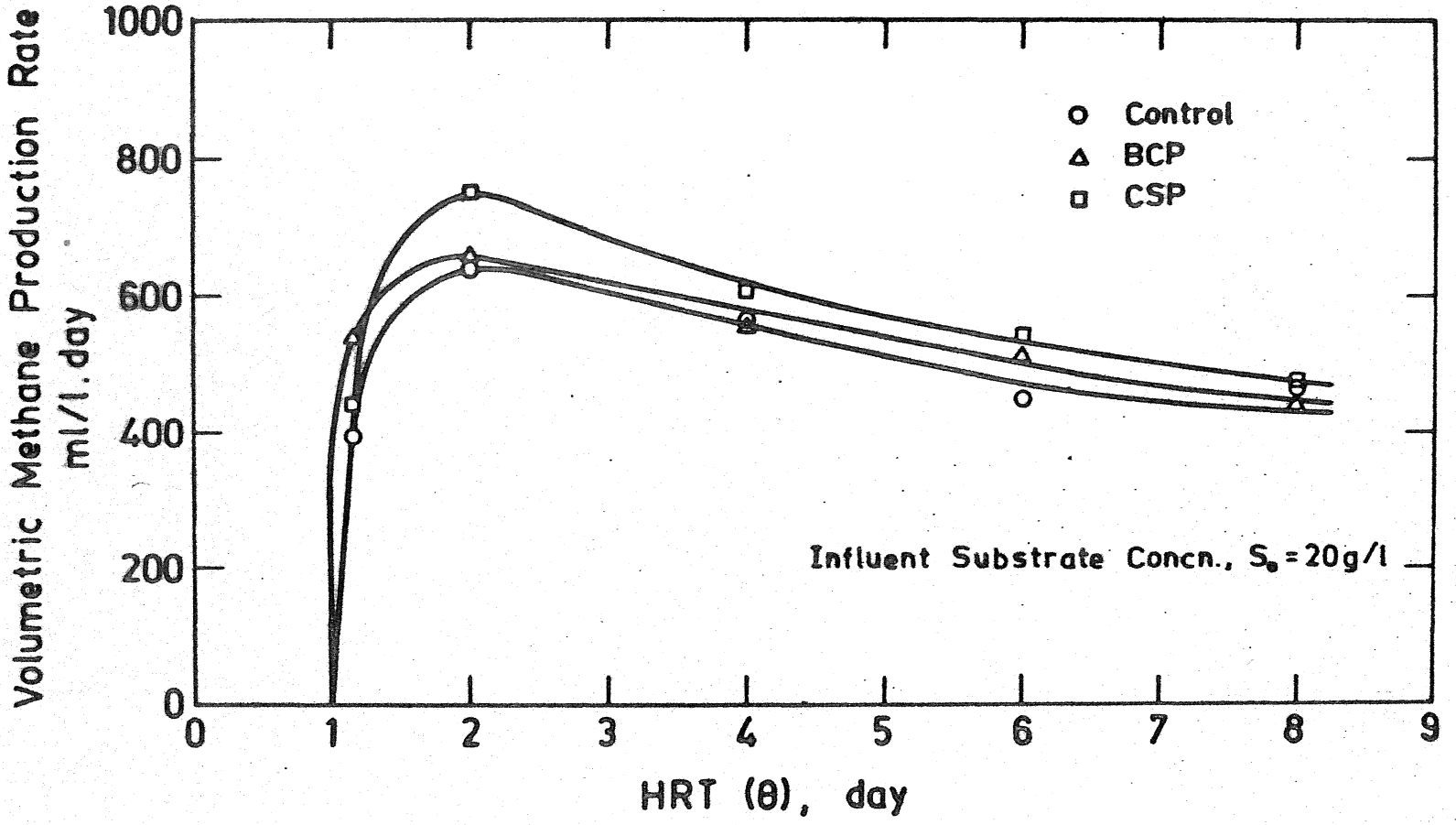


Fig. 5.5. Effect of HRT (θ) on Volumetric Methane Production Rate (G_s) with Different Additives. Molasses as Substrate.

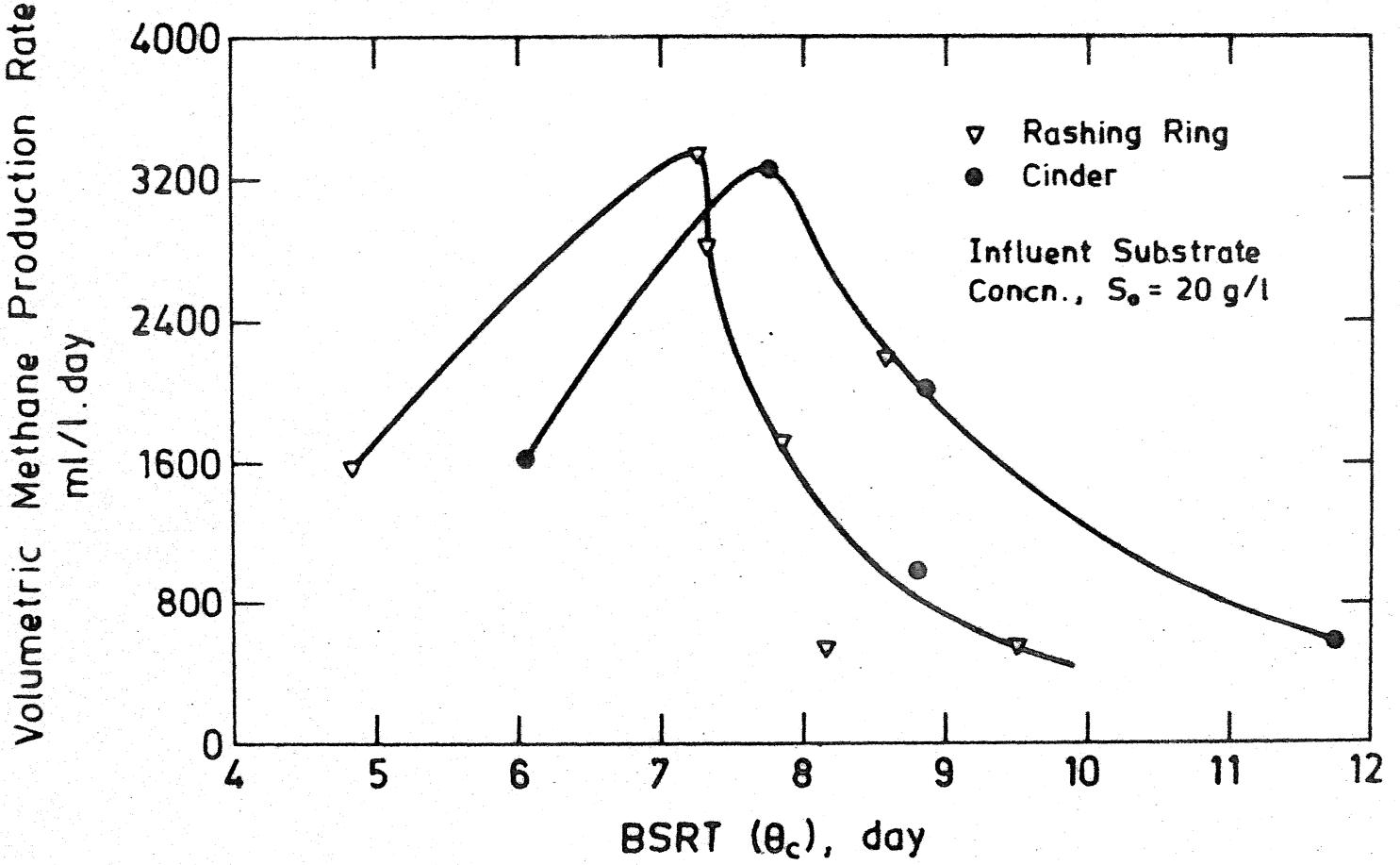


Fig. 5.6. Effect of BSRT (θ_c) on Volumetric Methane Production Rate (G_s). Molasses as Substrate.

Table 5.1. Evaluated Kinetic Constants for the Anaerobic System

Substrate	Type of surface added/ available	Influent load (S_o) g/l	From VFA data					From COD data		
			K_s, mg/l as CH_3COOH	μ_m day^{-1}	θ^m day	Y	K_d day^{-1}	K_s, mg/l as COD	μ_m day^{-1}	θ^m day
Molasses	No surface	20.0	5012	0.625	1.6	0.05	0.025	38666	0.87	1.15
	Coal	20.0	2784	0.57	1.75	0.041	0.025	31212	0.76	1.3
	Coconut	20.0	3370	0.58	1.72	0.041	0.025	48648	0.90	1.1
	Rashing ring	20.0	5012	0.625	1.6	0.05	0.025	38666	0.87	1.15
	Cinder	20.0	5012	0.625	1.6	0.05	0.025	38666	0.87	1.15
Glucose	No surface	20.0	3218	0.425	2.35	0.033	0.015	6885	0.42	2.377
	Coal	20,0	3909	0.43	2.3	0.033	0.02	12028	0.51	1.96
	Coconut	20.0	4771	0.49	2.04	0.038	0.17	8205	0.424	2.36
	Rashing ring	20.0	1892	0.43	2.3	0.03	0.02	2500	0.42	2.37
	Cinder	20.0	1122	0.43	2.3	0.29	0.02	2000	0.42	2.37

Contd...

Table 5.1 (continued)

Substrate	Type of surface added/ available	Influent load (S_o) g/l	From gas data							
			B_o ml CH_4/g COD	K_H	μ_m day^{-1}	θ^m day	From graph		From calculation	
							θ_{Gmax}	G_{max} ml CH_4/l day	θ_{Gmax}	G_{max} ml CH_4/l day
Molasses	No surface	20.0	204	1.002	0.622	1.60	2	640	3.21	626
	Coal	20.0	208	0.998	0.606	1.60	2	650	3.3	629
	Coconut	20.0	214	0.999	0.649	1.54	2	745	3.08	696
	Rashing ring	20.0	101	5.882	0.612	1.63	1	3300	5.6	104
	Cinder	20.0	160	1.333	0.666	1.50	1	3660	3.23	460
Glucose	No surface	20.0	194	1.000	0.393	2.54	6	520	5.68	318
	Coal	20.0	315	1.005	0.384	2.60	6	680	5.22	603
	Coconut	20.0	333	1.004	0.380	2.63	6	780	5.31	627
	Rashing ring	20.0	107	1.666	0.416	2.40	1	4620	5.5	170
	Cinder	20.0	123	2.220	0.360	2.77	1	4720	6.91	142

performance. The values of kinetic constants evaluated as per procedure of Chen and Hashimoto (1978) indicate the combined activity of the different species of methanogens producing methane from both the acetoclastic and hydrogen oxidising reactions.

5.1.5.1. Kinetic Constant for Suspended Growth Systems (Molasses Fed Digesters)

For the digesters receiving 20 g/l of molasses, the maximum growth rates observed were 0.625, 0.57 and 0.58 for control, BCP and CSP respectively from VFA data. The corresponding yield coefficients are 0.05 for control and 0.041 both for BCP and CSP. The decay rate in all the systemsremains same i.e. 0.025 per day. The reduction in μ_m for BCP and CSP from control should give lower growth rate of microbes for the identical substrate concentration, i.e., lower μ and this should result in production of more gas. An examination of Table 5.1 with regard to maximum gas production reveals that there is slight increase in gas for BCP and CSP digesters than control. Since the values of BCP and CSP are not much different than the control, it can be concluded that the presence of additional surface does not affect the maximum growth rate, yield coefficient and decay rate. Similar trend in μ_m values has been observed from COD data. The higher values of μ_{max} from COD data may be because it represent the overall system. The μ_{max} values from gas production data also reflects the same value as that from VFA data. The variation in μ_m values for different additives is not considerable, specially with VFA and gas data. Hence

it can be stated that the μ_{max} values for a particular type of substrate does not change with the addition of fine surfaces additives. The value of μ_{max} and K_s reported by Grasius (1983) for the system similar to control digesters are slightly higher in the present case when obtained from VFA and gas data, whereas, these are same for COD data. Higher value of K_s indicate a relatively lower performance of the present system when compared with that of Grasius (1983). Probably it may be due to high levels of VFA which has resulted in high μ_{max} and lesser gas production.

5.1.5.2. Kinetic Constants for Attached Growth Systems

The values of μ_{max} and K_s obtained for RR and cinder digesters fed with molasses are same as control digester. Similar observation with COD data is evident from the Table 5.1. The values obtained from COD data were higher than that obtained from VFA data. The reason for it may be same as explained above as in the case of suspended growth system. μ_{max} values for VFA and gas data were observed to be almost same. The values of θ_c^m for this system only reflect the biomass in suspended form which may not be taken as true representation of θ_c^m because of the attachment phenomenon. It is evident from Table 5.1 that the calculated values of maximum gas formation are less in case of RR and cinder than the experimental value. This may be due to limitations of equations 2.4.17 and 2.4.18 to predict the gas production in attached growth system. The value predicted by these equations appear to be valid

only for suspended system, since there is not much variation between predicted and experimental values in the case of BCP and CSP digesters.

The results, when compared with the 20 g/l glucose fed digesters show the higher values of μ_m for all types of digesters. As reported by Grasius (1983) the higher load of glucose may be inhibitive for methane formers. Since in this case 20 g/l of molasses is equivalent to 16 g/l of glucose on the basis of BOD to COD ratio (0.8), the probable cause can be absence of inhibition for molasses digesters whereas glucose fed digesters, organisms were subjected to some inhibition which resulted in low μ_m values for glucose.

5.1.3.3. Kinetic Constants for Glucose Fed Digesters

The results of μ_{max} values when compared for glucose fed digesters in the case of suspended growth systems (BCP and CSP) and attached growth system (RR and cinder), it was observed that μ_{max} values obtained from VFA, COD and gas data remain unchanged. K_s values for attached growth has been found to be less than that of control which represents better process stability. The values obtained for θ_{Gmax} and G_{max} from experimental data and calculations shows a significant difference in case of attached growth system. This may be due to continuous biomass build-up in the attached growth systems. In case of suspended growth system it is observed that calculated values shows G_{max} and θ_{Gmax} values to be slightly different. Similar reasons as discussed earlier can be putforth for this.

5.2. Treatability Studies

In order to obtain optimal organic loading schedule for anaerobic digestion with additives the experimentation was conducted by varying organic loadings from 3.3 Kg COD/m^3/day to a load at which the system starts failing. The process evaluating parameters used were VFA, methane production and COD removal. In this study it is also intended to arrive at a loading for which maximum gas production and maximum COD removal occurs.

5.2.1. Effect of Organic Loading on Methane Production

The steady state methane production at NTP in millimeters per litre of digesting liquid (ml/l) for each of the organic loading rates was determined for the molasses fed digesters, maintained at a HRT of 6 days. The pertinent results obtained using the different additives are presented in Figure 5.7. There is no significant enhancement in gas production for the digesters receiving BCP and CSP over the control digester.

Shelef et al. (1980) while treating poultry manure observed that using powdered and granular activated carbon as additives under mesophilic conditions could not increase the gas production. McConville and Mair (1978) reported that use of powdered activated carbon (PAC) while treating sewage sludges enhanced the methane production only by 10-15% at high detention times and resulted in a reduction of volatile suspended solids. Spencers (1978) reported enhancement of methane with PAC while coal and flyash powder have been found to be ineffective.

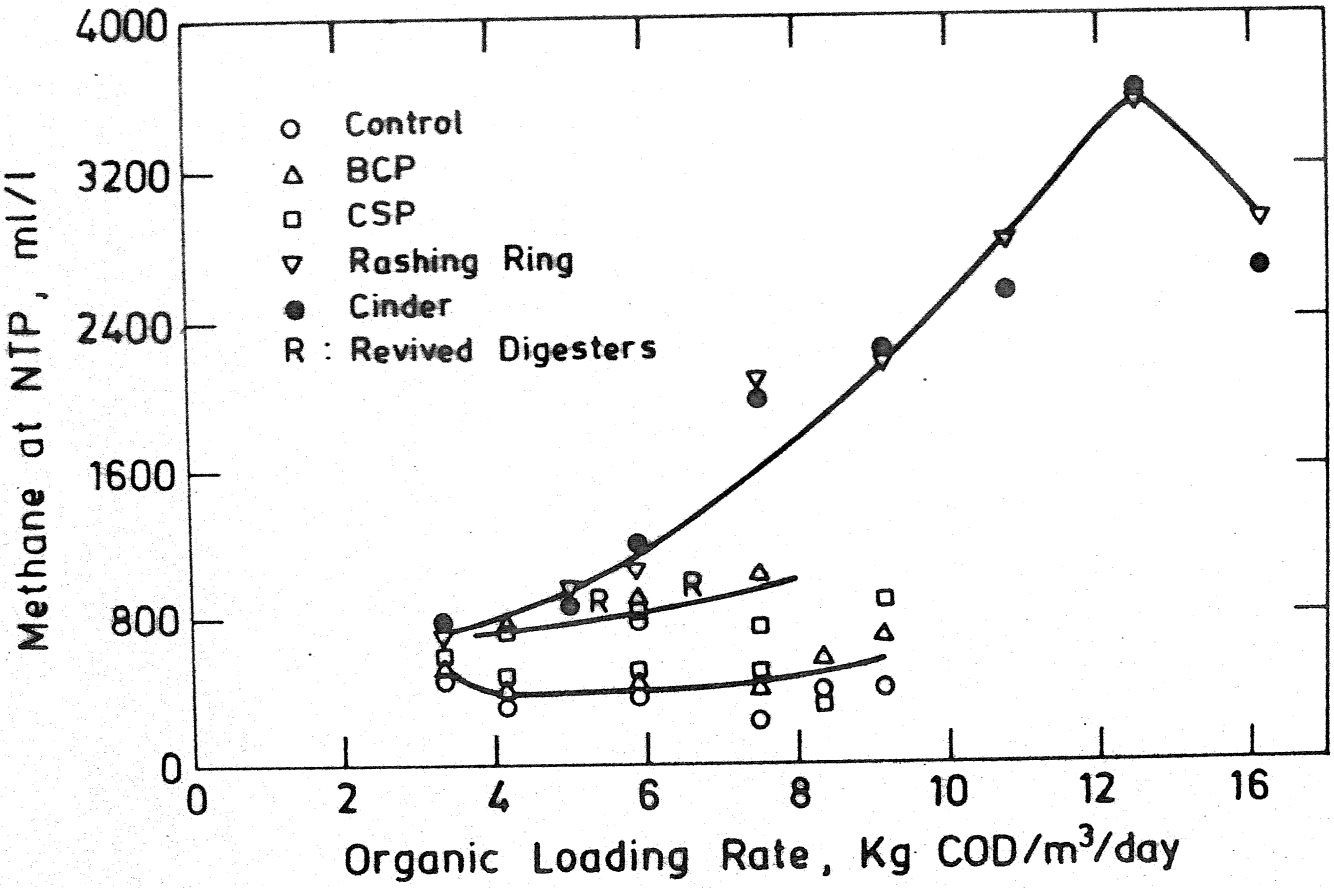


Fig. 5.7. Effect of Organic Loading Rate on Methane Gas Production in Molasses Digesters.

However, the digesters containing cinder and RR yielded higher methane production with the increase in organic load upto 12.5 Kg COD/m^3/day and beyond this loading a decline was observed. The powdered additives (size $\leq$85 µm) provide a larger surface area (0.41 m^2/g) than cinder (size passing 20 mm sieve and retained in 6 mm sieve) and RR (size 10 mm internal dia and 13 mm external dia) both of which provide a surface area of 0.04 m^2/l. However the effect of increased surface area with fine additives did not reflect in the enhanced gas production. It appears that the adhered microbes to the fine additives were also removed whenever effluent was withdrawn alongwith the additives, while, in the case of granular additives a biofilm was formed on its surface and when the effluent is withdrawn only suspended microbes are removed from the system. This has resulted in retaining higher biomass concentration in these reactors. The retention of biomass for the same HRT resulting in a higher BSRT is responsible for the significant enhancement in gas production for cinder and RR added digesters. The possible reason for this may be the accumulation of VFA beyond toxic limits, which inhibits the growth of methane formers.

The production of VFA as a function of organic loading presented in Figure 5.8, clearly depicts that there is an increase in VFA concentration for loads beyond 12.5 Kg COD/m^3/day for cinder and RR digesters. An interesting feature that can be observed is the sharp increase in VFA production even from the initial organic loading rate of 3.3 Kg COD/m^2/day for BCP, CSP and the control digesters.

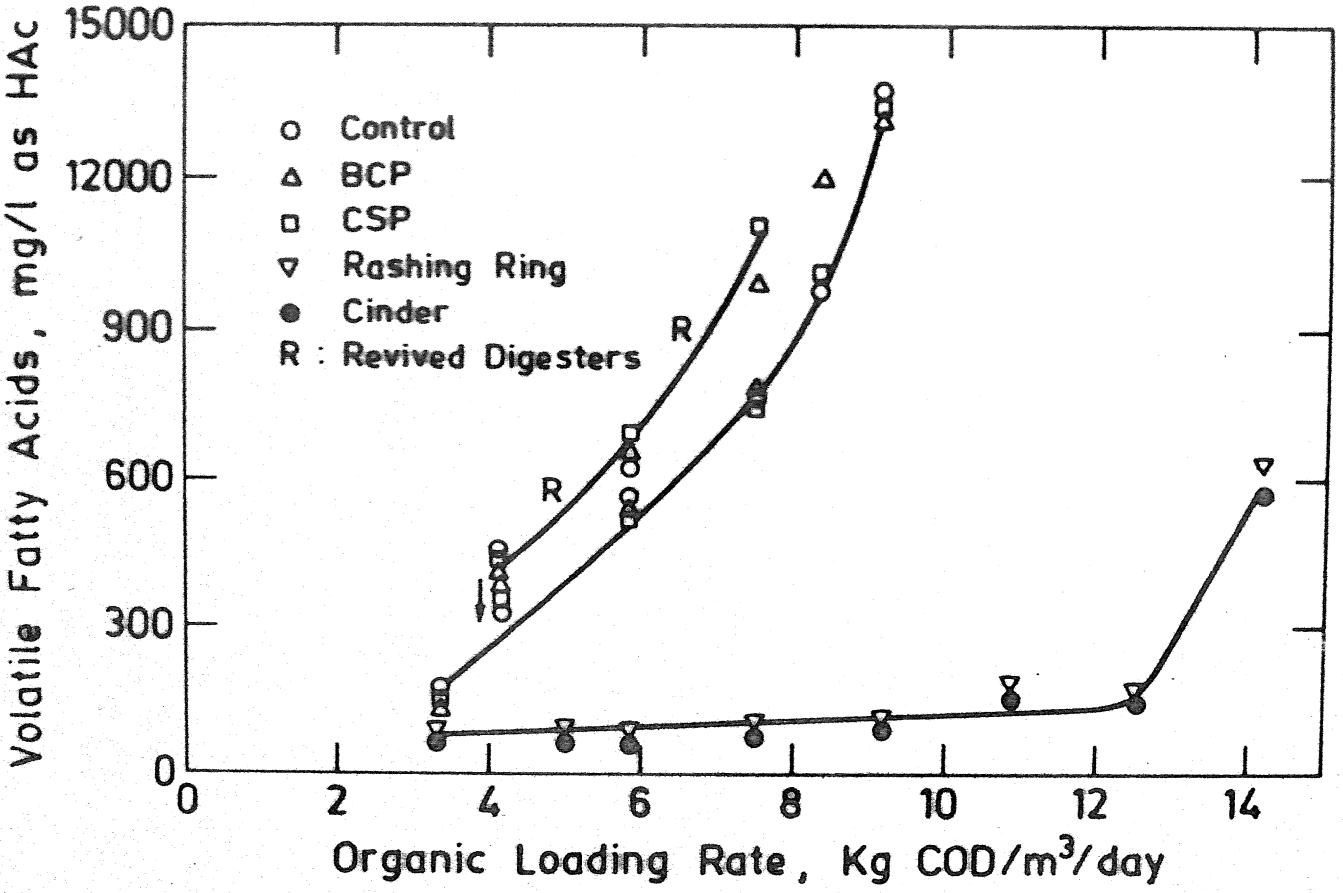


Fig. 5.8. Effect of Organic Loading Rate on Accumulation of VFA in Molasses Digesters.

This explains as to why there is no increase in gas production as against control for these digesters (Figure 5.7). The rate of production of VFA with respect to organic loading appears to follow first order equation in case of BCP and CSP digesters. The rate of methane production with respect to organic loading upto inhibitory loading can be determined by first order for RR and cinder digesters.

The results pertaining to methane production and VFA accumulation for various glucose fed digesters are presented in Figure 5.9. An enhancement of gas production in the cinder and RR digesters fed with glucose is observed to be similar to those fed with molasses. The accumulation of VFA and the resultant non-enhancement of gas in BCP and CSP digesters are also similar to those for molasses digesters. This confirms that more microbes are retained in cinder and RR added digesters than those with BCP and CSP added digesters. Organic loading in terms of COD represents completely biodegradable substrate. However, this is not true with molasses. The BOD/COD ratio for molasses as per Table 4.1 is 0.8. From this, organic loading rate of 5 Kg COD/m^3/day for glucose digesters is approximately equivalent to a load of 6.25 Kg COD/m^3/day for molasses digesters. Comparison of gas production at the above said loadings for glucose and molasses digesters reveals that molasses fed digester produce about 65 percent methane that of glucose digester. This may be due to the easy biodegradability of glucose and possible presence of toxic material in molasses for methane formers. In the digesters containing cinder and RR methane production

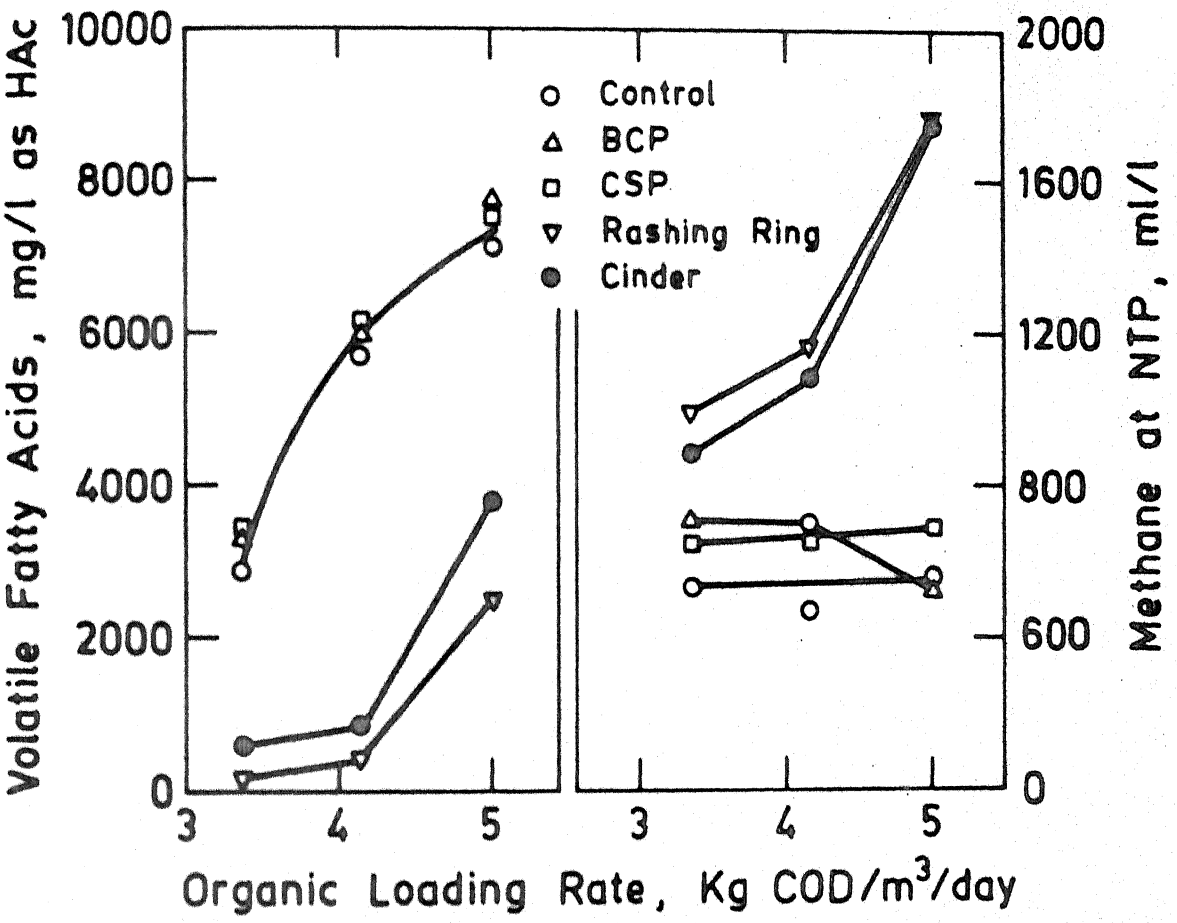


Fig. 5.9. Effect of Organic Loading Rate on VFA and Methane in Glucose Digesters.

rate was in the range of 0.18 to 0.283 m^3/Kg of COD destroyed for different organic loadings, which is about 51.4 to 81 percent of theoretical value of 0.35 m^3/Kg of COD (at NTP) as predicted by stoichiometry. The gas produced is approximately 2-3 times higher than that for BCP and CSP digesters and 2 to 4 times higher than the control digesters. Hickey and Owens (1981) using fluidized bed process for treating dairy waste which contained 'whole whey', recovered 92 percent of the theoretically extractable methane for a unit of COD removed. The maximum methane production rate of 3.54 l/l (Figure 5.8) was obtained at a load of 12.5 Kg COD/m^3/day in case of cinder and RR digesters fed with molasses. The percentage of methane in the off gas varied from 51-71.4 percent.

5.2.2. Effect of Organic Loading on Effluent Quality

The organic loading rates in the range 3.33 to 14.166 Kg COD/m^3/day were applied to digesters containing different additives. The COD removal ranged from 72 to 83 percent for cinder and rashing ring, and 65 to 25 percent for BCP and CSP digesters (Figure 5.10). The effluent VFA concentrations for cinder and RR digesters were low (Figure 5.8) upto a loading of 12.5 Kg COD/m^3/day corresponding to high removal of COD indicating that VFA contributed for COD. The COD removal for BCP and CSP digesters were low and corresponding increase in VFA is evident from Figure 5.8. The maximum COD removal (83 percent) for cinder and RR added digesters was obtained at an organic loading of 7.5 Kg COD/

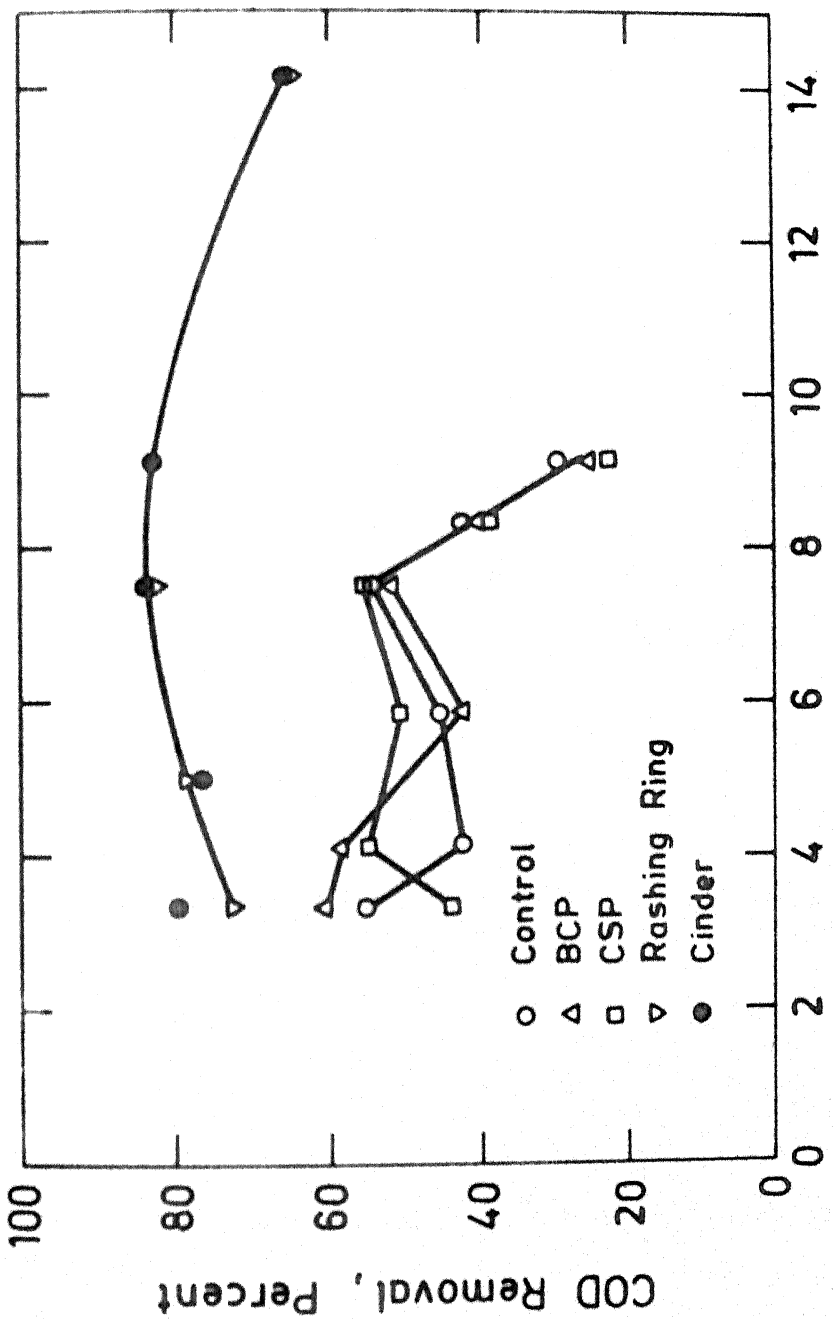


Fig. 5.10. Effect of Organic Loading Rate on COD Removal in Molasses Fed Digesters.

m^3/day, while maximum gas production was at a loading of 12.5 Kg COD/m^3/day.

5.2.3. Kinetics of Gas Production

The study to determine the quantity of gas produced as a function of time for 24 hrs after addition of substrate for those steady state attained digesters for organic loading was conducted. The kinetic data regarding gas production for digesters containing different additives and fed with molasses and glucose respectively at various loadings are presented in Figures 5.11 and 5.12, as specimen samples. As the loading is increased from 3.33 to 8.33 Kg COD/m^3/day the initial rate of methane production has doubled during first two hours after addition of molasses for BCP and CSP digesters (Figure 5.11). However, at the end of 24 hrs the net amount of gas produced for different loadings appears to be marginally different. Glucose fed digester also exhibited rather well defined similar trends in gas production, as evident from Figure 5.12. It can be said that the addition of BCP and CSP marginally improved the gas production. The data presented in Figure 5.11 for cinder and RR digesters fed with molasses clearly indicates very significant enhancement in gas production as compared to the control digester. For digesters fed with 5-8 COD/m^3/day the RR and cinder digesters produced 194 percent and 168 percent more gas than control, respectively. BCP and CSP digesters produced only 10 percent extra gas for the same loading .

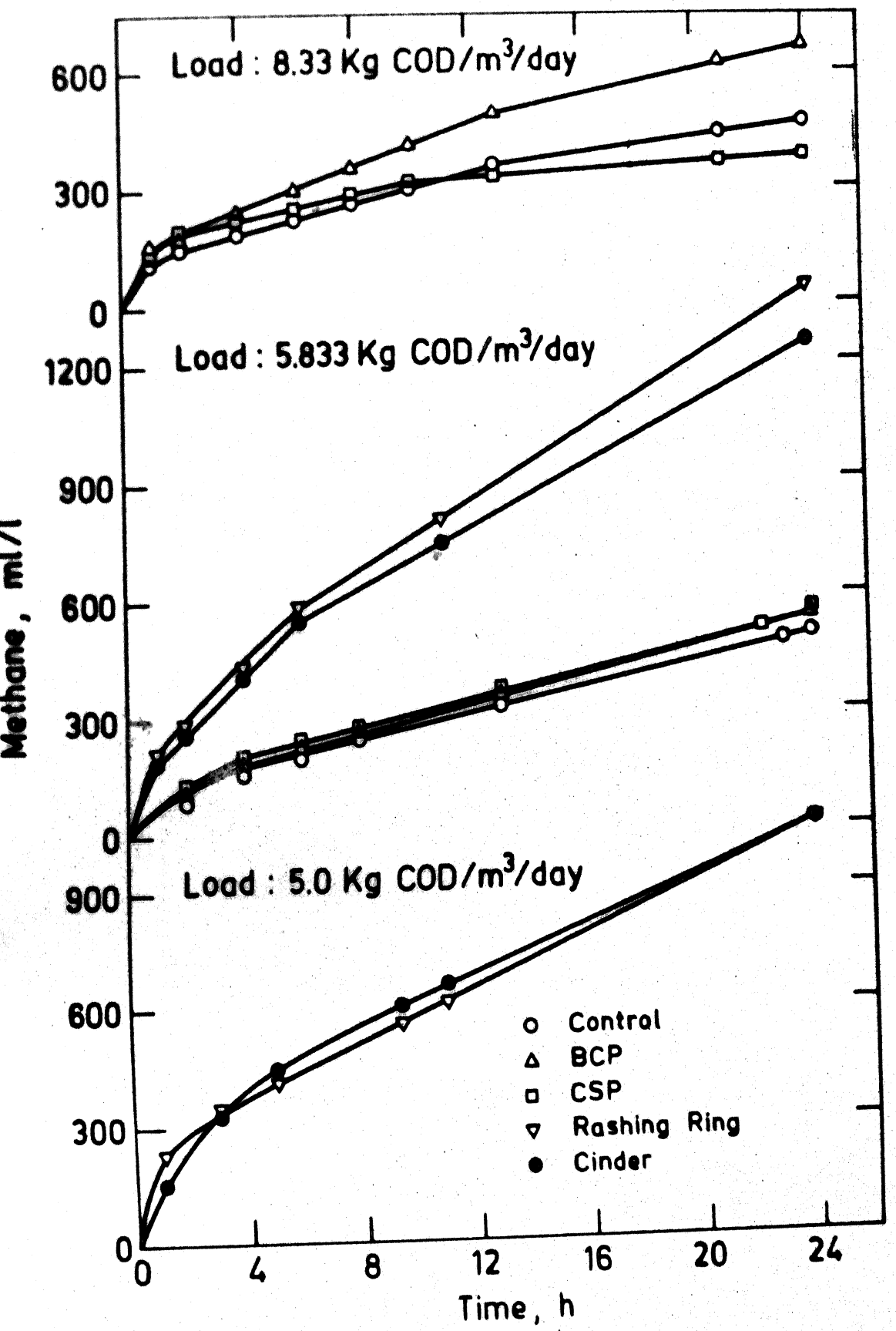


Fig. 5.11. Kinetics of Methane Formation in Molasses Digesters.

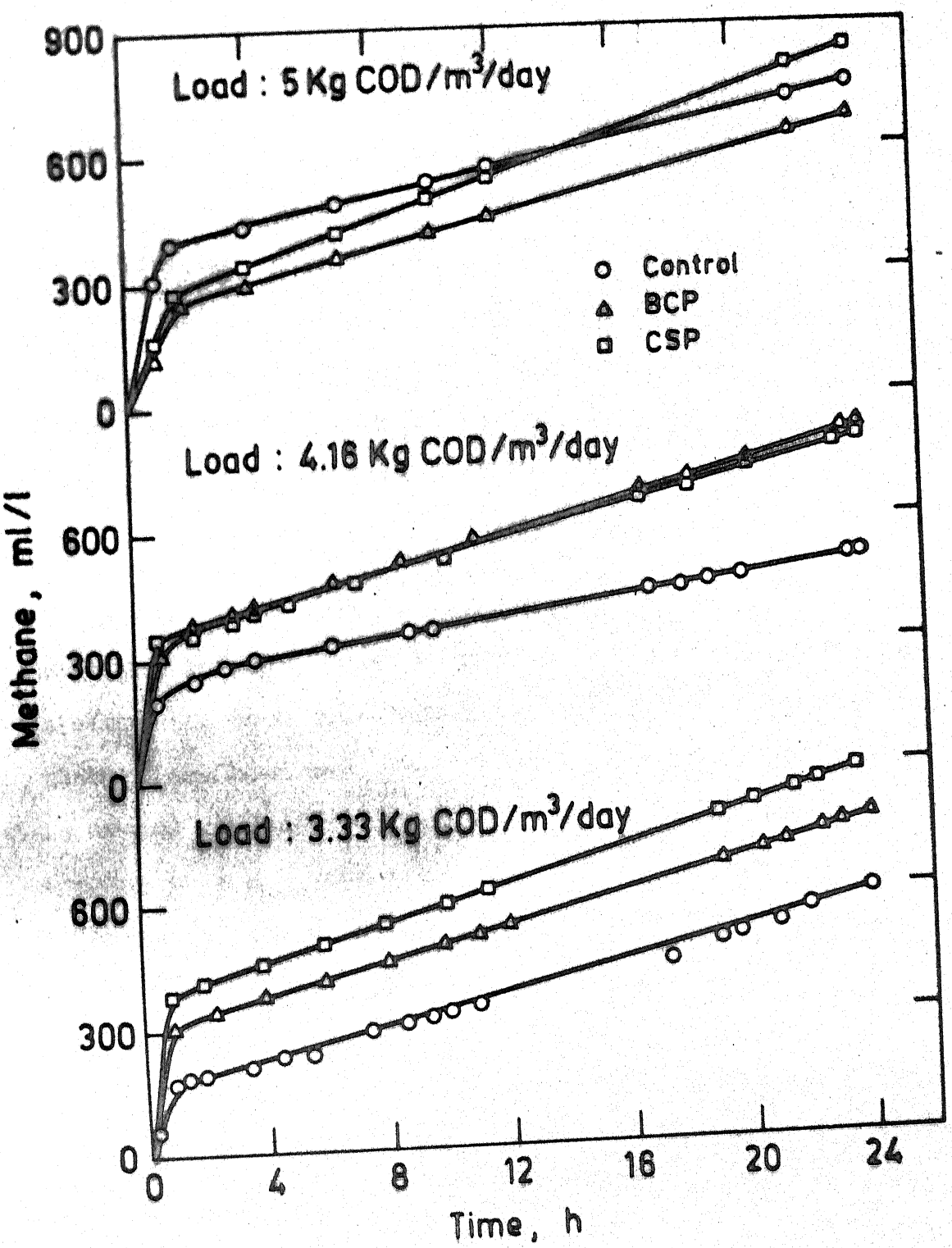


Fig. 5.12. Kinetics of Methane Formation in Glucose Digesters.

5.2.4. Study on Revival of Digesters

Digesters containing BCP, CSP and control when reived after their failure at a loading rate of 9.16 Kg COD/ m^3/day by starvation and alkali addition showed higher VFA levels as against first cycle at equivalent loading. This is evident from Figure 5.8 corresponding levels of methane were also observed to be almost double than first cycle of loading (Figure 5.7). The higher production of methane might be due to the acclimatisation of methane formers to the system. The trend of methane formation and accumulation of VFA was observed to be the same as in the first cycle.

5.2.5. Effect of Organic Loading on Biomass Concentration

In attached growth reactor, the production of more gas indicates that higher biomass is present in the system. In such system BSRT is much higher than HRT. An attempt has been made to find BSRT and biomass concentration in RR and cinder digesters fed with molasses. Taking into account that μ_{max} for a particular type of substrate is constant, K_s values were calculated for different loadings for the suspended system (control digesters). Using suspended growth system μ_{max} and K_s values corresponding to different substrate concentrations the value for attached growth systems were calculated for steady state VFA corresponding to initial substrate concentration for a HRT of 6 days. The BSRT (θ_c) values were then computed for RR and cinder digesters by taking reciprocal of above calculated values. It is possible to determine the biomass concentration

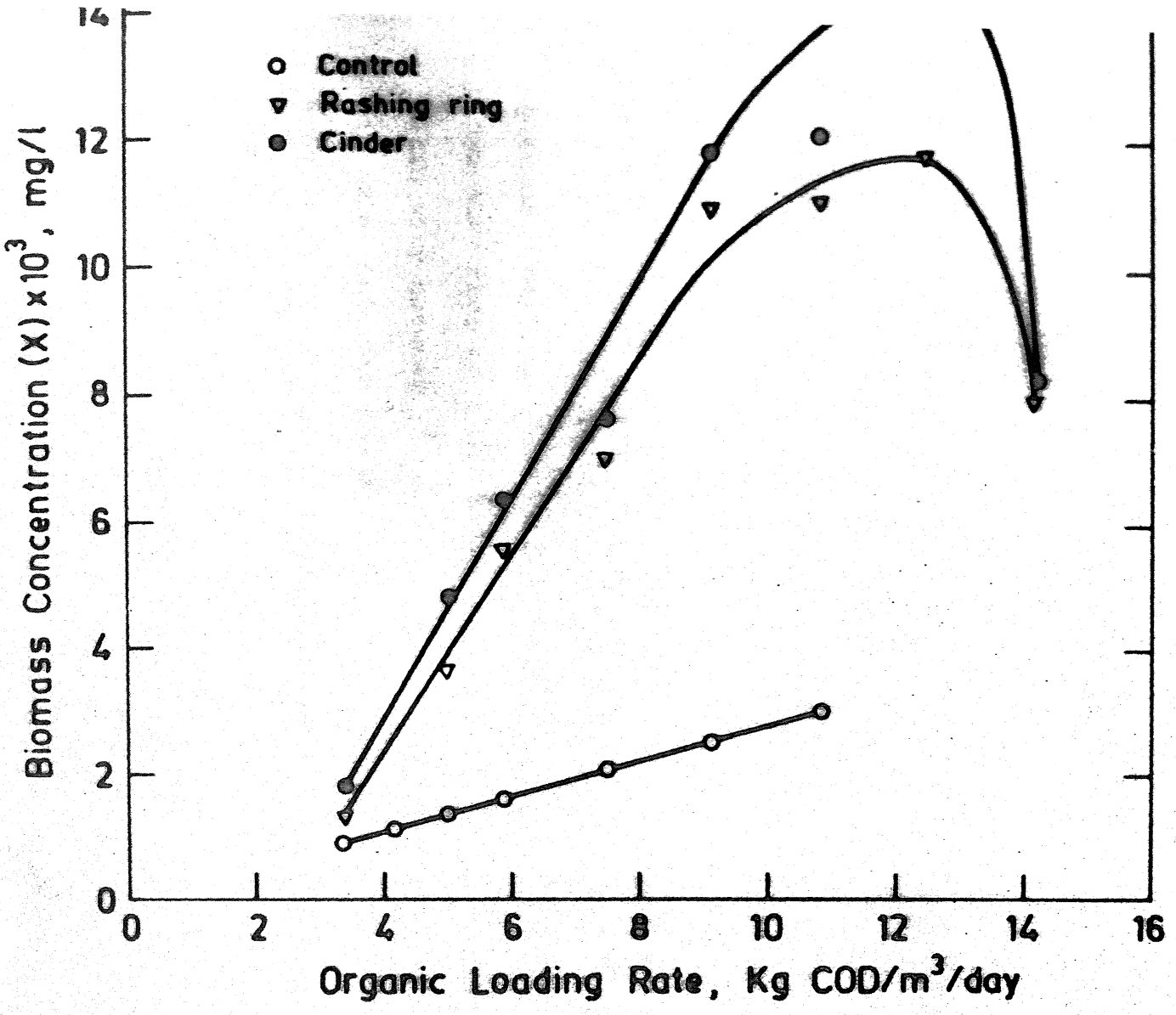


Fig. 5.13. Effect of Organic Loading Rate on Biomass Concentration (X) in Molasses Fed Digesters.

$$\frac{1}{\theta_c} = Y_T \cdot \frac{Q S_o}{V X} - K_d \qquad 5.4$$

Knowing concentrations and feed rate of influent, digesters capacity and using computed Y_T and K_d values, it is possible to determine the biomass concentration (X) in the reactor. In the case of cinder and RR digesters, the X value corresponds to the attached biomass. The results regarding biomass concentration as function of influent molasses concentration beside BSRT and μ values for control, cinder and RR digesters are presented in Table 5.2. In the control digester the μ value remains constant as BSRT is approximately equivalent to HRT. The biomass concentration increases by 3 times with three times increase in load. The maximum θ_c/θ ratio for cinder and RR digesters are respectively 9.8 and 12 percent. Harremoes and Henze (1982) have reported for an anaerobic fluidized bed biological reactor (AFBBR), the θ_c/θ ratio vary between 10 to 100. This enhancement makes anaerobic treatment with fixed film or attached growth systems economically interesting as compared to that with suspended growth anaerobic processes. Further, Hickey and Owen (1981) reports 92 percent extraction of theoretically available energy from Kg of COD of whey wastes using AFBBR while this investigation reveals that mere addition of cinder to the digester can yield 81 percent of theoretical energy with 12.5 Kg COD/m^3/day of molasses without any input energy as in AFBBR.

As per Figure 5.13 with increase in loading, coarse surface additives digesters have shown a rapid increase in

Table 5.2. Effect of Increase in Organic Loading on Biomass Concentration

Loading		Control				Rashing rings			Cinder		
mg/l	$Kg/m^3/day$	HRT θ day	Specific growth rate* $\mu.day^{-1}$	K_s mg/l	Biomass X mg/l	Specific growth rate $\mu.day^{-1}$	BSRT θ_c day	Biomass X mg/l	Specific growth rate $\mu.day^{-1}$	BSRT θ_c day	Biomass X mg/l
20,000	3.33	6	0.156	5012	922	0.103	9.7	1302	0.071	14.04	1736
25,000	4.166	6	0.156	10648	1153	-	-	-	-	-	-
30,000	5.0	6	0.156	13348	1386	0.044	22.72	3630	0.0264	37.88	4873
35,000	5.833	6	0.156	17127	1614	0.0274	36.50	5577	0.0213	46.94	6312
45,000	7.5	6	0.156	23785	2075	0.0284	35.21	7036	0.0189	52.91	8559
55,000	9.166	6	0.156	41085	2537	0.017	58.82	10934	0.0137	73.00	11867
65,000	10.833	6	0.156	45794	2998	0.0243	41.15	11009	0.02	50.00	12061
75,000	12.5	6	0.156	50502	-	0.021	47.62	11800	0.0178	56.18	14632
85,000	14.16	6	0.156	55211	-	0.064	15.62	7974	0.06	16.66	8350

* Value of maximum specific growth rate (μ_{max}) was taken as 0.625.

biomass as against control digester. The decrease in biomass after attaining a peak may be due to the inhibition of methane formers because of rapid increase in the VFA concentrations (Figure 5.8). The concentration of biomass was found to increase at a constant rate with increase in loading for the control digester. The variation in the biomass concentration observed at higher loading may be attributed to the shearing of the biofilm. The increase in biomass concentration to the extent of 3 to 5 times for digesters containing cinder and RR has resulted in enhancement of gas formation, low levels of VFA and better effluent quality. In AFBBR it has been reported that the biomass concentration is in the range of 10-40 g/l (Binot et al., 1982) whereas in cinder and RR digester it varied in the range of 12-14 g/l.

6. SUMMARY AND CONCLUSIONS

This study was directed to evaluate the effect of low cost additives such as bituminous coal powder (BCP), coconut shell powder (CSP) and rashing rings (RR) and cinder in granular form, for enhancement of gas production and to assess the treatability of a high strength BOD waste (molasses) under anaerobic conditions. The kinetic parameters for the design of reactors for rate limiting step of methanogens were obtained when the additional surface area for the growth of microbes was provided in the powdered and granular form. For comparison of these parameters a control digester, without additives was maintained. The semi-continuous reactors without sludge recycle were employed. The kinetic constants were evaluated from VFA, COD and gas data. The results were compared with the values obtained from a simple substrate as glucose. On the basis of this study following conclusions may be drawn.

1. The low cost additive like cinder, and rashing rings in granular form when added to the molasses fed digesters, enhanced the methane production by two to four times that of control digester for the same load, whereas BCP and CSP containing digesters showed only marginal improvement. By employing granular additives it was possible to extract 51 to 81 percent of theoretically available energy as against 38 percent of control digesters per Kg of chemical oxygen demand destroyed.

2. The gas production was 168 percent and 194 percent more for cinder and RR containing digesters respectively than control and enhancement was only by 10 percent for BCP and CSP digesters, treating molasses. The maximum methane production of 0.28 m^3/Kg of COD destroyed was obtained when the digesters containing cinder and RR were subjected to a molasses loading of 12.5 Kg COD/ m^3/day.

3. The higher methane production in the RR and cinder containing systems was because of the attachment of biomass on coarse surface. The θ_c/θ value have been found to be 9.8 and 12.1 respectively for RR and cinder digesterstreating molasses. The biomass concentration was found to be 3 to 5 times more in these digesters than control.

4. The COD removal ranged from 72 to 83 percent for reactors containing cinder and RR, while treating molasses whereas it averaged to 45 percent for BCP, CSP and control digesters. The maximum COD removal of 83 percent was obtained at loading of 7.5 Kg COD/m^3/day for cinder and RR digesters.

5. The lower levels of VFA resulted in better stability of the process in cinder and RR digesters than either control or digesters containing BCP and CSP.

6. The maximum specific growth rate μ_{max} has been found to be nearly constant irrespective of additional surface area available. It was in the range of 0.57 to 0.625 per day as evaluated by VFA data and 0.6 to 0.66 per

day as per gas data. The valuation of constants from gas data appears to be consistant. The values of K_d and Y also remains unchanged.

7. The minor variation in μ_{max} values obtained from different data such as VFA, COD, gas formation, can be due to the fact that the constants from VFA data reflects on the growth of acetoclastic bacteria, COD data yields for overall system and from gas data it represents the acetoclastic and hydrogen oxidising bacteria.

7. ENGINEERING SIGNIFICANCE

With the energy crises at hand and worse to come, a treatment system encompassing energy conversion while controlling the environmental pollution will always be preferred. For high BOD wastes, the choice of treatment thus should focuss on anaerobic digestion because of large amount of energy produced in the form of methane gas. For the efficient and economical design of reactors for desired degree of treatment and energy recovery, it is necessary to know the kinetic parameters which are dependent not only on the biological system of microbes but also on nature of waste, loading rate, temperature, pH etc. The present study can be utilised for the design of such reactor system where a complex waste having high BOD is to be treated. The provision of surface area for the growth of microbes using low cost materials like cinder seems to be a promising proposal for enhanced energy production and a better treatability, besides providing better process stability of the system. Consequently the higher organic loading that the process can take results in the reduction of the volume of the reactor. Based on θ_c/θ value for attached systems, the volume of digester containing cinder can be reduced by a factor of 6 to 7.

8. SUGGESTIONS FOR FUTURE INVESTIGATIONS

Based on the present work the following suggestions for the future investigations are made.

1. Effect of different sizes of coarse material to optimise the grading of material.
2. Pilot plant studies should be carried out using cinder or other low cost materials as a source of additional surface area for the growth of microbes.
3. Studies may be undertaken to investigate the kinetics of substrate inhibition beside inhibition due to its complexity and toxicity.
4. Mathematical models can be developed for finding the maximum gas production and minimum detention time for attached growth system.
5. The suitability of addition of locally available low cost materials for treatment of low BOD waste.

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APPENDIX I. Steady State Effluent Data - Influent Substrate (Glucose) Concentration Remains Constant, S_o = 20 g/l

Type of surface added/ available	Detention time in days	Effluent COD mg/l	VFA as CH_3COOH mg/l	Total gas ml/l/d	Methane ml/l/d at 37°C	Percentage of methane	ml of CH_4 at NTP per litre	ml of CH_4 of COD add removed
Control	8	2746	1188	1170	360	30.8	317	119
Coal	8	3661	1643	1205	700	58.1	617	231
Coconut shell	8	2983	1531	1250	695	55.6	615	230
Control	6	4921	2855	1290	590	45.7	520	146
Coal	6	6445	3245	1500	770	51.4	678	191
Coconut shell	6	7695	3410	1405	900	64.3	793	223
Rashing rings	6	3520	1530	1466	467	32.0	314	117
Cinder	6	2080	1200	1667	507	29.0	449	127
Control	4	16593	6184	1380	240	18.0	212	40
Coal	4	16980	5908	1430	315	22.0	278	52
Coconut shell	4	18346	5878	1563	215	14.0	190	36
Rashing rings	4	3680	2600	2300	1000	43.0	887	166
Cinder	4	2880	1475	2467	1360	55.0	1205	226
Control	2.67	18590	7517	2035	175	9.0	154	20
Coal	2.67	17562	6785	2050	315	15.3	278	35
Coconut shell	2.67	16528	6653	1785	315	17.7	278	35
Rashing rings	2.67	4260	3330	3530	1740	49.0	1548	193
Cinder	2.67	3680	3468	4000	2000	50.0	1771	222
Control	2	17600						
Rashing rings	2	8800	2913	4866	2133	44.0	1891	189
Cinder	2	8000	2400	5200	2400	46.7	2127	213

Contd...

APPENDIX I (continued)

Type of surface added/ available	Detention time in days	Effluent COD mg/l	VFA as CH_3COOH mg/l	Total gas ml/l/d	Methane ml/l/d at 37°C	Percentage of methane	ml of CH_4 at NTP per litre	ml of CH_4 of COD ad removed
Rashing rings	1.6	-	3052	6533	2800	42.8	2482	199
Cinder	1.6	-	1948	6733	2946	43.8	2612	209
Rashing rings	1.3	8000	3564	7933	3266	41.2	2895	188
Cinder	1.3	7200	2970	8666	3066	37.0	2718	177
Rashing rings	1	6400	3564	9400	5200	55.3	4609	231
Cinder	1	5600	3564	9933	5333	53.6	4727	237

APPENDIX II. Steady State Effluent Data - Influent Substrate (Molasses) Concentration Remains Constant, S_o = 20 g/l

Type of surface added/ available	Detention time in days	Effluent COD mg/l	VFA as CH_3COOH mg/l	Total gas ml/l/d	Methane ml/l/d at 37°C	Percentage of methane	ml of CH_4 at NTP per liter	ml of CH_4 or COD ad removed
Control	8	11362	1413	1050	530	50.7	467	187
Coal	8	10416	1285	1070	510	42.7	450	180
Coconut shell	8	11363	1294	1040	530	51.0	467	187
Control	6	8028	1670	995	510	52.7	450	136
Coal	6	7737	1210	1000	590	58.7	520	158
Coconut shell	6	11128	1309	980	620	63.3	546	166
Rashing rings	6	5700	1232	1167	600	51.4	532	162
Cinder	6	4800	788	1226	614	50.0	544	165
Control	4	14534	4066	1240	640	51.6	564	113
Coal	4	17441	4265	1150	625	54.4	551	110
Coconut shell	4	18895	4065	1260	685	54.4	604	121
Rashing rings	4	4960	1011	1667	660	39.8	585	117
Cinder	4	3200	1136	1933	1147	59.0	1016	203
Control	2.67	36585	8682	2015	415	20.6	366	49
Coal	2.67	44715	8802	1795	352	19.6	310	42
Coconut shell	2.67	32520	8794	1755	485	27.7	427	57
Rashing rings	2.67	6693	2506	3000	1733	57.7	1537	205
Cinder	2.67	5905	1818	3066	1760	57.3	1560	208

Contd...

APPENDIX II (continued)

Type of surface added/ available	Detention time mg/l	Effluent COD mg/l	VFA as CH_3COOH mg/l	Total gas ml/l/d	Methane ml/l/d at 37°C	Percentage of methane	ml of CH_4 at NTP per liter	ml of CH_4 of COD ad removed
Control	2.0	34552	8537	5542	725	13.0	639	64
Coal	2.0	42682	8545	5610	740	13.2	652	65
Coconut shell	2.0	40650	8227	5690	850	14.9	749	75
Rashing rings	2.0	8000	1142	5060	2533	50.0	2245	225
Cinder	2.0	6830	1147	4800	2200	45.8	1950	195
Control	1.33	-	9017	3460	450	13.2	396	26
Coal	1.33	-	8728	3550	610	17.2	537	35
Coconut shell	1.33	-	8837	3450	500	14.5	440	29
Rashing rings	1.33	5400	1380	8666	3200	38.4	2836	185
Cinder	1.33	3200	1335	7600	3200	42.1	2836	185
Rashing rings	1.00	6400	1437	7240	3733	51.6	3310	166
Cinder	1.00	4800	1335	7800	4133	53.0	3663	183

APPENDIX III. Steady State Effluent Data - (HRT Remains Constant) - Glucose Concentration, S_o = 20-30 g/l

Type of surface added/ available	Load COD $Kg/m^3/d$	Influent COD mg/l	Effluent COD mg/l	VFA at CH_3COOH mg/l	Total gas ml/l/d	CH_4 (at 37°C) ml/l/d	Percentage CH_4	CH_4 at NTP ml/l/d	m^3 of CH_4 per Kg of COD added at NTP	Percentage CO removed
Control	3.33	20000	4921	2855	1383	613	44.27	539.83	0.16211	75.39
Coal	3.33	20000	6093	3245	1437	790	54.95	695.70	0.20891	69.53
Coconut shell	3.33	20000	6875	3410	1400	737	52.73	649.03	0.19490	65.62
Rashing rings	3.33	20000	3089	274	2130	1120	52.58	986.3	0.296	84.5
Cinder	3.33	20000	2114	517	1950	1030	51.28	580.6	0.264	89.4
Control	4.17	25000	13954	5787	1510	535	35.45	471.14	0.1284	44.2
Coal	4.17	25000	11240	6022	1715	800	46.62	704.51	0.1691	55.0
Coconut shell	4.17	25000	12984	6090	1726	780	45.75	686.9	0.1649	48.06
Rashing rings	4.17	25000	-	432	2600	1294	49.63	1140.0	0.2735	-
Cinder	4.17	25000	-	804	2506	1240	45.48	1090.0	0.2621	-
Control	5.0	30000	11570	7131	1803	625	35.20	559.2	0.1118	61.43
Coal	5.0	30000	11776	7766	2006	605	30.14	532.8	0.1066	60.74
Coconut shell	5.0	30000	11363	7694	1952	800	39.99	704.6	0.1409	62.12
Rashing rings	5.0	30000	-	2506	3893	2000	51.37	1761.2	0.3522	-
Cinder	5.0	30000	-	3802	3253	2000	61.48	1761.2	0.3522	-

APPENDIX IV. Steady State Effluent Data - (HRT Remains Constant) - Molasses Concentration, S_o = 20-85 g/l

pe of sur-ce added/ ailable	Load COD $Kg/m^3/d$	Influent COD mg/l	Effluent COD mg/l	VFA at CH_3COOH mg/l	Total gas ml/l/d	Methane ml/l/d at 37°C	Percen-tage of methane	CH_4 at NTP ml/l/d	m^3 of CH_4 per Kg of COD $x10^{-3}$ added/ removed	Percentage COD removed
ntrol	3.33	20000	8928	1676	980	510	51.77	449.13	135	55.36
al	3.33	20000	7936	1223	1005	590	58.70	519.58	156	60.31
conut shell	3.33	20000	11178	1369	980	620	63.26	546.00	164	44.11
shing rings	3.33	20000	5440	996	1370	797	58.90	706.4	212	72.80
nder	3.33	20000	4160	650	1400	817	59.30	724.0	218	79.20
ntrol	4.16	25000	14345	3542	975	410	42.05	361.06	87	42.62
al	4.16	25000	10330	3806	965	395	40.93	348.0	84	58.67
conut shell	4.16	25000	11270	3652	1055	420	39.81	370.0	88	54.92
ntrol	5.00	30000	17047	4440	1467	460	31.30	407.7	92	43.17
shing rings	5.00	30000	6932	1008	2067	1080	52.24	957.2	192	78.69
nder	5.00	30000	7049	588	1973	1043	52.80	924.5	185	76.50
ntrol	5.83	35000	19084	5698	1220	475	38.93	418.3	78	45.47
al	5.83	35000	20038	5678	1100	520	47.27	458.0	79	42.74
conut shell	5.83	35000	17175	5512	1350	530	39.25	466.7	80	50.96
shing rings	5.83	35000	-	783	2360	1173	51.20	1040.0	178	-
nder	5.83	35000	-	604	2402	1334	55.50	1182.4	203	-
ntrol	7.50	45000	20325	7712	1967	210	10.41	185.0	25	54.83
al	7.50	45000	21341	7725	1930	460	23.84	405.0	54	52.57
conut shell	7.50	45000	20325	7460	2060	550	26.70	484.0	65	54.83
shing rings	7.50	45000	8000	1102	3320	2373	71.40	2090.0	279	82.22
nder	7.50	45000	7500	723	3615	2195	60.76	1933.0	258	83.33

Contd...

APPENDIX IV (continued)

Type of surface added/ available	Load COD $Kg/m^3/d$	Influent COD mg/l	Effluent COD mg/l	VFA at CH_3COOH mg/l	Total gas ml/l/d	Methane ml/l/d at 37°C	Percentage of methane	CH_4 at NTP ml/l/d	m^3 of CH_4 per Kg of COD $x10^{-3}$ added/ removed	Percentage COD removed
Control	8.33	50000	28585	9979	2390	460	19.24	405.09	48	42.83
Coal	8.33	50000	30522	12090	2280	660	28.90	581.22	70	38.95
Coconut shell	8.33	50000	29061	10027	2450	368	15.00	324.07	39	41.88
Control	9.17	55000	38617	13666	3260	445	13.65	391.8	43	29.80
Coal	9.17	55000	28455	12920	3280	800	34.39	704.56	77	48.26
Coconut shell	9.17	55000	28682	13431	3305	1005	30.40	855.04	97	22.40
Rashing rings	9.17	55000	-	1129	4772	2432	50.90	2155.63	235	-
Cinder	9.17	55000	9500	921	4812	2468	51.30	2187.54	239	82.72
Control	10.83	65000	-	15233	2576	810	31.80	718.0	66	-
Rashing rings	10.83	65000	-	1854	5383	3146	58.45	2788.0	257	-
Cinder	10.83	65000	-	1544	5987	2846	47.54	2523.0	233	-
Rashing rings	12.50	75000	-	1760	6063	3983	65.69	3530.0	282	-
Cinder	12.50	75000	-	1479	6572	4000	60.85	3545.0	284	-
Rashing rings	14.17	85000	28985	6303	8011	3286	41.01	2912.0	205	65.9
Cinder	14.17	85000	28985	5820	7633	3005	39.38	2663	187	65.9

APPENDIX V. Steady State Effluent Data for Revived Digesters - (HRT Remains Constant) - Molass
Concentration, S_o = 25-95 g/l

Type of surface added	Load COD Kg/m3/d	Influent COD mg/l	VFA as CH_3COOH mg/l	Total gas ml/l/d	Methane ml/l/d at 37°C	Percentage CH_4	CH_4 at NTP ml/l/d	m^3 of CH_4/Kg of COD added at NTP
Control	4.166	25000	4504	2020	930	46.00	819	0.1966
Coal	4.166	25000	4131	1840	900	48.90	793	0.1902
Coconut shell	4.166	25000	4534	1700	860	50.58	757	0.1818
Control	5.833	35000	5468	2200	890	40.45	784	0.1343
Coal	5.833	35000	6599	2050	1100	53.65	968	0.1660
Coconut shell	5.833	35000	7006	1870	1000	53.47	880	0.1510
Control	7.5	45000						
Coal	7.5	45000	9900	2500	1160	46.4	1021	0.1362
Coconut shell	7.5	45000	11100	2040	780	38.2	687	0.0915